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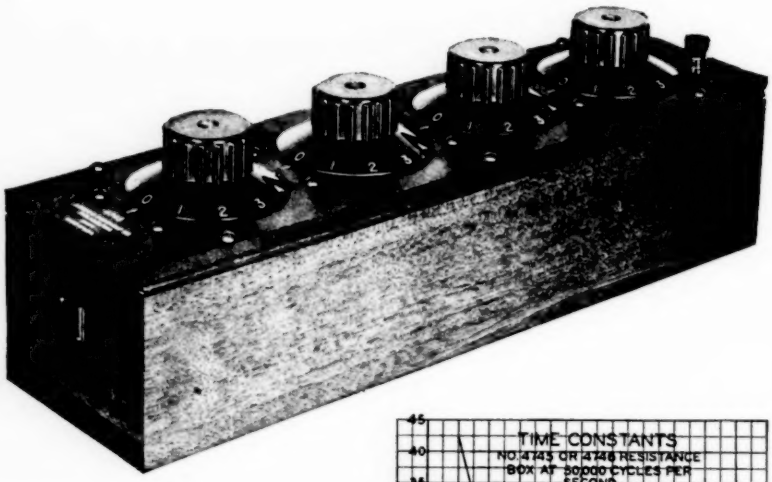
An article will not be accepted for publication in THE PHYSICAL REVIEW unless the manuscript is accompanied by an adequate abstract for publication at the beginning of the article. This abstract is intended to aid the reader by furnishing an index and a brief summary of the contents of the article. Besides serving these purposes it should also be suitable for reproduction in abstract journals so as to make it unnecessary for the editors of these journals to have another abstract prepared.

As *an index* it should be complete; all the subjects, major and minor, concerning which new information is presented, should each be given, with sufficient precision so that any reader can tell from the abstract whether the article contains anything of interest to him. The subject indexes of abstract journals are fundamental in reference work. These indexes are prepared exclusively from the abstracts and whatever is omitted from the abstracts cannot be included in the index and may thus be lost. The writer of an abstract should therefore feel himself under an important obligation to his scientific colleagues to make sure that the abstract is accurate and complete, at least as an index.

As *a summary* the abstract should give briefly the conclusions of the article, important advances in experimental technique and theory, and all numerical results of general interest that may be conveniently given including all that might belong in a handbook and table of contents. It should give all the information that readers who are not specialists in the particular field involved might desire to know about the article thus saving them the time and trouble in referring to the article itself. Experience has shown that in general the length of the abstract should be from four to eight percent of the length of the article.

THE PHYSICAL REVIEW, 1923-1925, contains many examples of adequate abstracts. Most of these contain paragraph titles and subtitles which indicate the subjects concerning which new information is given and it is required that authors include such subtitles when all the information contained in the article does not refer to the subject indicated by the title of the article. Such subtitles may be frequently avoided by rewording the title so as to make it more precise.



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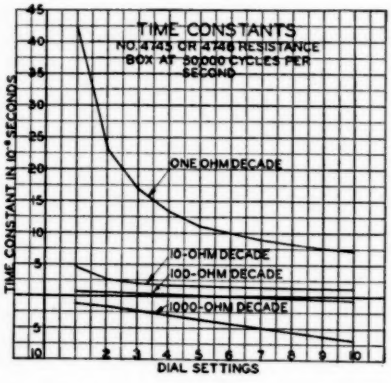

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PHYSICAL REVIEW

FURTHER EXPERIMENTS ON THE UNIFORMITY OF DISTRIBUTION OF THE COSMIC RADIATION

By Robert A. Millikan
California Institute of Technology

(Received December 8, 1931)

Abstract

More careful and prolonged observations on the small, daily variation before reported in the measured intensities of the cosmic rays, the new observations being made under such conditions as to eliminate the possibility of a slight temperature effect suggested by Bowen and Millikan's recent explanation of ionization-pressure relations in high-pressure electroscopes, yield the definite result that *within the limits of the author's present observational uncertainty which is of the order of a third of a percent, the sun has no direct influence on cosmic-ray intensities.* New evidence is presented that if observed and apparently systematic variations of the order of a third of a percent are in fact real they are best interpreted as the result of small changes in the blanketing effect of the earth's atmosphere due to air currents.

IN OCTOBER, 1930[1] I published briefly the results of a long series of tests designed to bring to light minute effects of the sun or the milky way or of other celestial objects on the intensity of the cosmic radiation. These experiments brought to light no evidence for any such effects, indeed definite evidence aaginst their existence; but they did reveal a slight daily period of the order of a percent and of such character as to be best interpretable in terms of daily changes in the thickness of the atmosphere through which the rays must pass to reach the earth's surface.

These observations were taken for the most part out-of-doors and at different altitudes up to 14,000 feet with a sensitive, high-pressure, cosmic-ray electroscope but in such a way as to eliminate completely the possibility of a temperature effect upon the elastic constants of the electroscope. Nevertheless there were other possibilities of temperature effects and since the just discernable maximum in the values of the comsic ray intensities seemed invariably to coincide with the period of maximum daily temperature as well as of minimum barometric pressure, I undertook during the past summer to repeat some of these measurements under conditions in which the temperature of the electroscope could be held very nearly constant.

A further reason for studying these daily variations with great care is

[1] R. A. Millikan, Phys. Rev. **36**, 1595 (1930).

found in the fact recently brought to light by Bowen and myself[2] that the lack of linearity in the ratio between pressure and ionization in high pressure electroscopes is due to the impossibility of obtaining saturation with ordinary potentials in the use of such instruments. Thus if the same beta-ray, for example, passes first through an electroscope at one atmosphere and second through a similar electroscope at thirty atmospheres, in the latter instance the detached electrons are separated from their mother atoms, let us say, one thirtieth as far as in the first instance. However the forces causing them to reunite vary rapidly with the distance apart and therefore become so huge in the second instance that it is impossible to obtain saturation with potentials anything like those which produce it easily at one atmosphere. In some experiments of my own less than half of the ions were caught at 30 atmospheres although with the use of potentials between 100 volts and 300 volts the currents had the appearance of saturation, i e., they were practically independent of the applied potential between these limits.

This explanation which Bowen and I have recently given of pressure-ionization effects obviously carries with it the conclusion that in such a high-pressure, unsaturated electroscope a somewhat larger number of ions will be carried to the electrodes at high temperatures than at low, since increased energy of agitation will obviously prevent a certain number of ions from reuniting that would otherwise do so. At 30 atmospheres this effect of temperature on current is not large for differences of temperature of say ten or fifteen degrees centigrade such as will sometimes occur between night and day; but in refined measurements it should be appreciable. It is a fundamental source of weakness in the use of high-pressure electroscopes. For measuring *relative* ionizations at constant temperature such high-pressure electroscopes are satisfactory, but for very fine measurements made at different temperatures they may lead to serious errors. This is presumably the cause of some of the differences in the results obtained by different observers on the variation of cosmic-ray intensities with the positions of celestial objects, inadequate precautions having been taken to avoid this effect of temperature on the measured ionization currents.

My own experiments made on Pike's Peak (altitude 14,100 feet) in both 1928 and 1930, (continued however through but two days) failed to reveal any daily period there; but they were made in a heated room of reasonably constant temperature while my experiments made out-of-doors both at Pasadena and at Gem Lake and on Mount Manitou (continued however over a period of many days and hence giving more significant mean values) showed clearly a maximum in the afternoon of the order of one per cent.

I therefore repeated during the past summer (July and August) the Pasadena measurements as follows. I divided the day into four equal six hour periods: (1) 6 A.M. to noon, (2) noon to 6 P.M., (3) 6 P.M. to midnight and (4) midnight to 6 A.M., these periods being purposely taken long so as to eliminate as far as possible the random fluctuations to be expected. The first series

[2] Bowen and Millikan, Nature, Oct. (1931).

of measurements was made in Throop Hall, California Institute, with several feet of concrete both above (in the floors) and in the side walls, but with the temperature varying but slightly, in general not more than one degree centigrade during the different periods. The second series was taken in the basement of my house at 1640 Oak Grove Avenue, Pasadena, with equally constant temperatures but with only wood above the instrument. The results are shown in Tables I to IV.

TABLE I. *Cosmic-ray intensity measurements in Throop Hall, Pasadena, July 11th to August 16.*

	Morning ions cc/sec.	Barometer inches	Afternoon ions cc/sec.	Barometer inches	Evening ions cc/sec.	Barometer inches	Night ions cc/sec.	Barometer inches
7/11	—	—	27.54	*29.06*	27.36	*29.06*	27.37	*29.07*
7/12	27.29	*29.06*	27.69	*29.03*	27.69	*29.04*	27.15	*29.05*
7/13	27.17	*29.04*	27.26	*29.02*	27.48	*29.01*	27.41	*29.03*
7/14	27.50	*29.04*	27.52	*29.00*	28.10	*29.03*	27.65	*29.04*
7/15	27.45	*29.03*	27.63	*29.02*	27.77	*29.09*	27.57	*29.09*
7/16	27.54	*29.07*	27.40	*29.09*	27.41	*29.12*	27.47	*29.12*
7/17	27.36	*29.11*	28.00	*29.06*	27.61	*29.03*	27.63	*29.04*
7/18	27.67	*29.02*	28.01	*28.99*	28.09	*28.98*	27.58	*28.99*
7/19	27.34	*28.99*	27.52	*28.98*	27.42	*29.00*	27.59	*29.04*
7/20	27.09	*29.03*	27.27	*29.00*	27.24	*28.99*	27.72	*29.02*
7/21	27.54	*29.03*	27.40	*29.00*	27.23	*29.00*	27.39	*29.02*
7/22	27.34	*29.01*	27.95	*28.99*	27.11	*28.98*	27.31	*29.00*
7/23	27.39	*28.98*	27.86	*28.95*	27.47	*28.93*	27.41	*28.95*
7/24	27.22	*28.95*	27.42	*28.93*	27.40	*28.94*	27.51	*27.97*
7/25	27.44	*28.96*	27.50	*28.95*	27.26	*28.96*	27.41	*28.97*
7/26	27.30	*28.97*	27.43	*28.92*	27.06	*28.93*	27.25	*28.97*
7/27	27.73	*28.95*	27.11	*28.95*	27.46	*28.98*	27.50	*29.01*
7/28	27.04	*29.02*	—	—	—	—	27.41	*29.04*
7/29	27.37	*29.03*	28.08	*29.02*	27.81	*29.04*	27.26	*29.07*
7/30	27.51	*29.06*	27.50	*29.04*	27.40	*29.06*	27.21	*29.09*
7/31	28.02	*29.08*	27.67	*29.04*	27.61	*29.05*	27.44	*29.08*
8/1	27.21	*29.06*	27.99	*29.03*	27.31	*29.02*	27.33	*29.03*
8/2	27.32	*29.03*	27.39	*29.00*	27.16	*29.02*	27.65	*29.05*
8/3	27.69	*29.05*	27.34	*29.04*	27.36	*29.06*	27.18	*29.10*
8/4	27.23	*29.09*	27.17	*29.08*	27.50	*29.09*	27.15	*29.11*
8/5	27.36	*29.11*	27.41	*29.08*	27.58	*29.09*	27.19	*29.14*
8/6	27.17	*29.15*	27.29	*29.12*	27.57	*29.15*	27.72	*29.19*
8/7	27.14	*29.17*	27.06	*29.19*	27.29	*29.14*	27.28	*29.18*
8/8	—	—	—	—	—	—	27.14	*29.20*
8/9	27.38	*29.20*	27.63	*29.16*	27.19	*29.17*	27.57	*29.24*
8/10	27.40	*29.22*	27.52	*29.17*	—	—	—	—
Means	27.387	*29.051*	27.528	*29.030*	27.461	*29.035*	27.415	*29.062*

It will be seen from Table 1 for example, that the divergence of the individual readings from the mean is in general less than a percent. It should be said too that these readings of about 27 ions per cc per second represent essentially pure cosmic-ray intensities, the local radiation, which itself was found to be here very constant, being practically all screened out by the completely encircling lead envelope, 7.6 cm in thickness. The zero reading of the electroscope is 1.2 ions per cc per sec. The readings in Tables I and III are uncorrected for changes in barometric height, but the mean barometer reading during each period is given in the column immediately to the right of the intensity reading in question.

The barometric height remains remarkably constant during the month of observations represented in Table I and the eight days of observation repre-

sented in Table III; but the barometer goes through a small minimum each afternoon and a small maximum in the morning hours. In other words the mean barometric heights during the periods from midnight to 6 A.M. and 6 A.M. to noon are always higher than during the periods from noon to 6 P.M. or from 6 P.M. to midnight; but the cosmic-ray intensities show just the in-

TABLE II. *Cosmic-ray readings, July 11 to August 10, Reduced to barometer of 29.04 inches.*

	Morning	Afternoon	Evening	Night
7/11	—	27.58	27.38	27.38
7/12	27.31	27.68	27.69	27.16
7/13	27.17	27.24	27.41	27.40
7/14	27.50	27.47	28.09#	27.65
7/15	27.44	27.61	27.83#	27.63
7/16	27.50	27.34	27.31	27.37
7/17	27.45	27.98#	27.60	27.63
7/18	27.65	27.95#	28.01#	27.52
7/19	27.28	27.45	27.36	27.59
7/20	27.08	27.22	27.18	27.70
7/21	27.50	27.35	27.18	27.37
7/22	27.30	27.89#	27.04#	27.26
7/23	27.32	27.75	27.33	27.30
7/24	27.11#	27.28	27.28	27.44
7/25	27.34	27.39	27.16#	27.32
7/26	27.21	27.28	26.92#	27.16
7/27	27.62	27.00#	27.39	27.46
7/28	27.02#	—	—	27.41
7/29	27.36	28.06#	27.81#	27.30
7/30	27.49	27.50	27.40	27.17
7/31	28.07#	27.67	27.62	27.49
8/1	27.22	27.98#	27.29	27.32
8/2	27.28	27.34	27.14#	27.64
8/3	27.70#	27.34	27.38	27.23
8/4	27.29	27.22	27.56	27.24
8/5	27.45	27.46	27.65	27.31
8/6	27.31	27.39	27.71#	27.91#
8/7	27.30	27.18#	27.41	27.46
8/8	—	—	—	27.34
8/9	27.58	27.78	27.35	27.77#
8/10	27.62	27.68	—	—
Means	27.394	27.515	27.446	27.331

verse of these relations. In both Tables I and II the afternoon mean-cosmic-ray-intensity is the highest, though only of the order of a third of a percent or less, while also in both tables the period 6 A.M. to noon shows the *minimum* mean intensity.

Both tables give indications that the differences in the means result from slight changes in the thickness of the atmospheric blanket due to the air currents set up by the daily heating of the earth's surface by the sun's rays. Indeed the differences cannot possibly be due to a *direct* influence of the sun since in both tables the maximum and the minimum mean readings both occur while the sun is up. The lag in all the effects after the period of maximum heating or cooling is indicated in both Tables I and III, the columns giving both barometric readings and ionization readings in the period 6 P.M. to midnight showing apparently that the atmospheric currents with their consequent changes in the atmospheric blanket, which reach their maximum in the afternoon, hold over also into the evening period (6 P.M. to midnight)

TABLE III. *Cosmic-ray measurements in basement of 1640 Oak Grove Avenue, Pasadena, August, 11–20, 1931.*

	Morning	Barometer	Afternoon	Barometer	Evening	Barometer	Night	Barometer
8/11	28.27	*29.27*	28.77	*29.25*	28.43	*29.28*	28.23	*29.29*
8/12	28.74	*29.29*	28.42	*29.29*	28.30	*29.30*	28.37	*29.32*
8/13	28.38	*29.32*	28.56	*29.32*	28.10	*29.33*	28.71	*29.34*
8/14	28.23	*29.34*	28.68	*29.29*	28.73	*29.28*	28.52	*29.30*
8/15	28.41	*29.26*	28.73	*29.24*	28.26	*29.26*	28.58	*29.28*
8/16	28.30	*29.27*	28.24	*29.24*	28.69	*29.24*	28.85	*29.27*
8/18	28.65	*29.23*	28.71	*29.20*	28.77	*29.22*	28.70	*29.24*
8/19	28.55	*29.23*	28.25	*29.20*	28.68	*29.21*	28.28	*29.26*
Means	28.441	*29.276*	28.546	*29.254*	28.494	*29.265*	28.530	*29.285*

while the quieter conditions which establish themselves between midnight and morning also seem to hold over into the period from 6 A.M. to noon.

For reasons which I have before given[1] the reduction of the readings in Tables I and III to a particular value of the barometric pressure cannot be expected completely to wipe out the differences in the means of the ionization

TABLE IV. *Cosmic-ray readings, August 11–20 reduced to barometric height of 29.26 inches.*

	Morning	T °C	Afternoon	T °C	Evening	T °C	Night	T °C
8/11	28.25	*24.8*	28.75	*24.7*	28.46	*24.5*	28.28	*24.2*
8/12	28.79	*24.4*	28.45	*18.6*	28.36	*24.5*	28.46	*24.1*
8/13	28.47	*24.4*	28.65	*24.3*	28.22	*24.1*	28.83	*24.1*
8/14	28.35	*24.3*	28.75	*24.5*	28.77	*24.3*	28.62	*23.9*
8/15	28.41	*24.3*	28.71	*24.9*	28.26	*24.5*	28.61	*24.0*
8/16	28.30	*24.6*	28.21	*25.1*	28.66	*24.4*	28.85	*23.6*
8/18	28.60	*24.2*	28.62	*24.8*	28.70	*23.9*	28.66	*23.0*
8/19	28.50	*23.4*	28.19	*24.6*	28.54	*24.5*	28.26	*23.6*
Means	28.459		28.541		28.496		28.571	

at different periods since the barometer must respond somewhat to both static and dynamic influences,[3] while if the incoming rays are actually constant, a cosmic-ray electroscope should reflect merely the total mean thickness of the blanket or air-wave interposed at a given time between the recording instrument and the rays coming in over the whole celestial dome, independently of whether the atmosphere is in motion or at rest. Tables II and IV represent such reduction of all readings to a common pressure. This is seen to reduce somewhat the differences between the means without however wiping them out. The relative positions of all the means in Table II remain the same as in Table I and this is true also of the morning, afternoon and evening means of Table IV but the "night mean" in Table IV has risen a trifle above that of the afternoon mean. This raises perhaps a little doubt as to whether all the differences may not be accidental, but the evidence on the whole seems to be rather in favor of a very slight afternoon maximum and a morning minimum occasioned by atmospheric currents due to solar heating.

[3] Chapman, Proc. Royal Soc., June (1931) concludes from theoretical considerations that these differences cannot amount to as much as one percent, while these new observations of mine show experimentally that they do not amount to more than about a third of a percent.

I have noted a bit of further evidence in this direction in Table II. The fluctuations in the individual readings seem in general to be somewhat less in the period from midnight to 6 A.M. than during the other three periods, and this is the period in which the atmosphere is normally most quiet. In Table II, I have starred every reading which differs from the mean at the bottom of its column by as much as 1 percent. If the fluctuations are all due to changes in the thickness of the atmospheric blanket the "night" column should show the smallest number of such stars as it will be seen to do in Table II. There is definite evidence however, brought to light both by Steinke in Germany and by Carl D. Anderson in Pasadena for occasional wholly random bursts of ionization due to something like catastrophic nuclear disintegrations and it is therefore at least a possibility though not a likelihood that all of the apparent regularities in the mean differences (Tables II and IV) are accidental.

The only *certain* conclusion that I can draw from the whole set of observations is then that *within* the *limits of my own observational uncertainty, which has now been reduced to about a third of a percent, the sun has no direct influence upon the intensity of the cosmic rays.* I can make the same assertion on the basis of other only partially published data with respect to the milky way and also with respect to the nearest spiral nebula, Andromeda. The foregoing result is also in complete agreement with the extraordinarily careful and exact observations of Hoffman in Halle. The foregoing statement is the same as that which Cameron and I made as a result of our observations in Bolivia and on the Pacific Ocean between Los Angeles and Mollendo Peru, in 1926, but the limit of our uncertainty was then estimated at 6 percent while it has now been reduced to about a third of one percent. With this precision attained and with the great difficulty, if not the entire impossibility, of making dependable allowances for the effect of small waves in the atmosphere as well as for the effect of random fluctuations in ionization, great caution must clearly henceforth be exercised in interpreting any results as showing minute variations either with solar or with sidereal time.

COSMIC-RAY IONIZATION AND ELECTROSCOPE-CONSTANTS AS A FUNCTION OF PRESSURE

By Robert A. Millikan
Norman Bridge Laboratory of Physics
California Institute of Technology
Pasadena

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Abstract

1. The residual ionization in an electroscope at infinite depth in water, that is, its zero reading, is found to be an inverse function of the pressure. Thus, in a particular electroscope the zero at 1 atmosphere was 5.13 ions cc/sec., while at 30.1 it had fallen to 1.2 ions cc/sec.

2. Also, when in this electroscope the pressure was changed from 1 atmosphere to 30.1 atmospheres the observed ionization current rose but 13.80 fold, which multiplying factor was found the same for gamma rays and for cosmic rays.

3. Both of these pressure effects are shown to be due to lack-of-saturation in high pressure electroscopes, as first explained in Nature of October 3, 1931, by Bowen and the author.

4. From the multiplying factor found in (2) in the measured ionization at Pasadena in this 30 atmosphere high-pressure electroscope, the number of cosmic-ray ions at 1 atmosphere (24° C 74 cm pressure) in this electroscope at Pasadena is found to be fairly accurately 2.63 ions cc/sec.

5. The sea level value of the ionization in this electroscope is 2.48 ions cc/sec.

I. Introduction

WHEN in the fall of 1926 after our return from our experiments in Bolivia, Dr. Cameron and I set about increasing the sensibility of our cosmic-ray electroscopes through the use of high pressures we at first assumed that, at least up to the pressures we then wished to use, about 10 atmospheres, the ionization produced by rays of the enormous penetrating power of the cosmic rays would be proportional to pressure.

When, however, at Arrowhead Lake, we took ionization-depth curves down to depths of 200 feet with the same electroscope, first when filled to a pressure of one atmosphere, then to a pressure of from 6 to 8 atmospheres, and a little later to a pressure of 30 atmospheres, we found two unexpected results, first, a marked dependence of the zero of the electroscope, i.e., the reading which it asymptotically approached at great depths, upon pressure, and second, a markedly smaller ionization current at high pressures than corresponded to the expected linear relation between pressure and ionization. The chief purpose of the present paper is to present and explain these findings.

II. Electroscope Zero a Function of Pressure

With respect to the zero of the instrument the following data are illustrative. In effect three depth-ionization curves were first taken with the same electroscope at three different pressures, namely 1 atmosphere, 4.56 atmospheres, and 6.66 atmospheres. This particular electroscope will be called electroscope No. 1. It was spherical, capable of being completely encased in a

spherical lead screen 7.6 cm thick, and had a volume of 1580 cc. The rate of discharge when completely evacuated was taken and found to be quite negligible, corresponding to a few tenths of a division per day or less than 0.2 ion per cc per second, so that although the leak of the supports is included in the zero anyway and is therefore eliminated, there is no possibility of its introducing appreciable uncertainty into the measurements by its variability. The zero of the instrument is then defined as the asymptotic value of the measured ionization current toward which the readings approach at infinite depth. It is due to traces of radioactive impurities in the walls. These asymptotic values were found in the case of electroscope No. 1 to be as follows:

At 1 atmosphere, zero reading = 3.50 ions cc/sec.
At 4.56 atmosphere, zero reading = 2.20 ions cc/sec.
At 6.66 atmosphere, zero reading = 1.97 ions cc/sec.

In the case of electroscope No. 2(Vol. 1610 cc), which was made precisely as was No. 1 of steel hemispheres 0.66 mm thick, each carrying a flange at the equator for the sake of air-tight bolting, only zero pressure and atmospheric pressure were used, the former for seeing that the leaks of the supports were negligible and the latter for taking ionization readings. This electroscope, too, could be encased in lead 7.6 cm thick. The zero at one atmosphere of this electroscope was found by the foregoing method to be 3.73 ions cc/sec., and by a completely independent and more exact method (see below) to be 3.91 ions cc/sec. Although the difference is 5 percent I probably cannot claim a greater accuracy than this in this particular zero determination.

In the case of electroscope No. 3, which had a volume of 1622 cm and a wall thickness of 3 mm of steel, depth-ionization curves were taken at one atmosphere and at 30 atmospheres. The latter is the curve published in the Physical Review 37, 235(1931). It is of course very much more dependable than any of the other curves since under the influence of the same radiation the currents are 13.8 times as great as at one atmosphere. This means that the asymptotic value can here be determined with relatively great precision, and in addition this zero value is so low (1.2 ions per cc/sec.) that a large percentage of error in it would affect but little the following computations or the conclusions drawn from them.

Let x be the zero value at 1 atmosphere, r_1 the reading in the electroscope at one atmosphere at any depth where the ionization is large enough so that the percentage error in it is small, say at 1 meter below the water surface, and let R_1 be the reading at this same depth where the pressure in the electroscope is 30 atmospheres. Also let R_{35} and r_{35} be the corresponding readings at a relatively large depth, say 35 meters. Then obviously

$$\frac{R_1 - 1.2}{r_1 - x} = \frac{R_{35} - 1.2}{r_{35} - x}.$$

Testing this equation to see whether x comes out constant when other readings than those at 1 m and 35 m are used is equivalent to proving that the actual cosmic-ray depth-ionization curve is independent of the type of electroscope used for testing it. When in one case the readings at 1 m and 20 m

beneath the surface and in a second case at 0.85 cm and 35 m were substituted the zero of electroscope No. 3 at one atmosphere came out 5.13 ions cc/sec. and 5.12 ions cc/sec., respectively. The zero of electroscope No. 3 was then taken as 5.13 at one atmosphere and 1.2 at 30 atmospheres.

The foregoing method of comparing depth-ionization curves with different electroscopes was actually used in fixing all the above mentioned zero-values. A check-method on the foregoing determinations is as follows. After fixing the zero of No. 3 at 5.13 ions cc/sec., the three electroscopes 1, 2, and 3 were set up in the same spot on the campus at Pasadena all enclosed in the same lead shield. The mean ionization current in No. 1 was found to be 5.51 ions cc/sec., in No. 2 was 5.96 ions cc/sec., and in No. 3 it was 7.18 ions cc/sec. Then since the same external radiation is operating in all cases the zero of No. 1 must be the zero of No. 3 minus $(7.18-5.51)$ or $5.13—1.67=3.46$ ions cc/sec. as against 3.5 mentioned above as determined by the first method. Similarly the zero of No. 2 is $5.13-(7.18-5.96)=3.91$ as against 3.73 as determined from the under-water work at Arrowhead.

The foregoing data sufficiently establish the dependence of the electroscope-zero upon pressure. The reason for this dependence is obviously that increase in pressure reduces in much the same proportion the distance of separation of electrons detached from atoms by the radioactivity in the walls. And, since the forces pulling the detached electrons back to the parent atom vary inversely with a high power of the distance apart, ions which can get to the electrodes at low pressures cannot do so at high. In other words, *saturation becomes impossible at high pressures even though the applied potential is much increased, since the recombining forces increase enormously more rapidly.*

Although the foregoing explanation was seen at once to be satisfactory for the case of the relatively soft rays coming from radioactive constituents in the walls, it was not at once evident that it should also apply to the ionization produced by the extraordinarily penetrating cosmic rays. Indeed, the nature of the ionization produced by the cosmic rays was completely unknown so that the following facts were discovered purely experimentally.

III. Number of Cosmic-Ray Ions Produced in Electroscope No. 3 at Pasadena

For the sake of finding the ionization produced in electroscope No. 3 at one atmosphere by the cosmic rays the following procedure was adopted, Electroscope No. 3 was set out on a stand under a tree on the campus of the California Institute at Pasadena and a series of readings taken alternately with and without the lead envelope. These readings were

	Without Pb	With Pb
July 11, 1928	11.67	7.39
July 12, 1928	11.50	7.12
July 13, 1928	11.67	7.02
		7.20
Means	11.61	7.18

The zero of this electroscope having been determined as 5.13 by the underwater work at Arrowhead Lake (altitude 5,100 feet) it follows that $11.61-5.13=6.48$ = total ions formed per cc/sec. at Pasadena. (altitude 756 feet) and that $7.18-5.13=2.05$ = total ions inside Pb formed per cc/sec. at Pasadena.

But now from the general cosmic-ray curves in lead and in water already published by Cameron and myself[1] and taken with this same electroscope at 30.1 atmospheres it will be seen that the percentage of the cosmic rays getting through this identical lead screen at Pasadena is

$$(28.2-1.2)\div(37.5-1.2)=74.4 \text{ percent}$$

Hence approximately $2.05\div 0.744=2.75$ cosmic-ray ions per cc/sec. are formed at Pasadena (alt. 756 ft. above sea level) in electroscope No. 3 when it is not surrounded by lead. Hence, approximately of the 6.48 ions all told formed in electroscope No. 3 at Pasadena 2.75 are due to cosmic rays and $6.48-2.75=3.73$ are due to radioactivity in the earth and air. These figures need the following correction. Of these radioactive rays 2.4 percent get through the lead and there produce 0.09 ions so that of the 2.05 ions inside the lead only $(2.05-0.09)=1.96$ are really of cosmic origin. Hence the ions due to cosmic rays in No. 3 electroscope when it is outside the lead are $1.96\div 0.744=2.63$ and those due to local radioactive gamma-rays are $6.48-2.65=3.85$. The first of these numbers is constant within less than a percent[2] the second is of course variable in many localities, but in the dry summer months at Pasadena it was not found to vary by more than the limits of uncertainty of these measurements of it.

IV. Multiplying Factor for Cosmic Rays at 30 Atmospheres Same as for Gamma-Rays

Now in order to get the multiplying factor by which the ionization currents due to cosmic rays in electroscope No. 3 are increased when the pressure is raised from 1 atmosphere to 30 atmospheres it is only necessary to take as above from the general cosmic-ray curve obtained in water by Cameron and myself[1] with this electroscope at this pressure, the value of the ionization in it at the altitude of Pasadena. This is seen to be $(37.5-1.2)=36.3$ ions. Dividing this by the number of ions formed by the same cosmic rays when the electroscope has a pressure of 1 atmosphere, namely 2.63, one obtains as *the cosmic-ray multiplying factor for 30 atmospheres 13.80.*

It is interesting to compare this with the multiplying factor for ordinary gamma-rays of radium and thorium. This can be obtained as follows: The difference between the ionization currents observed with electroscope No. 3 at 1 atmosphere has been given as $11.61-7.18=4.43$. This difference represents almost wholly the radioactive gamma-rays that are cut out by the lead. The same experiment was made in the same spot when the pressure was thirty atmospheres, the mean reading without lead being 90.75 ions cc/sec. and with

[1] Millikan and Cameron, Phys. Rev. **37,** 244 (1931).
[2] Millikan, Phys. Rev. **39,** 391 (1932).

lead 29.75 ions cc/sec. The ionization current now produced by these same rays is then.

$$90.75 - 29.75 = 61.00$$
$$61 \div 4.43 = 13.79$$

i.e., *the multiplying factor is the same for cosmic rays as for gamma-rays. This result is of no little importance since it means that the mechanism of ion formation with cosmic rays is essentially the same as with gamma-rays.*[3]

Since gamma-rays and cosmic rays show the same multiplying factor[4] it is of course unnecessary in order to get this factor to separate the ionization into the part due to cosmic rays and the part due to gamma-rays. Thus we had the total ionization at one atmosphere in No. 3 at Pasadena as $11.61 - 5.13 = 6.48$. Similarly at thirty atmospheres the total ionization is $90.75 - 1.02 = 89.55$. The multiplying factor for all the rays cosmic and gamma, is then $89.55 \div 64.8 = 13.82$. The beautiful agreement between these three different ways of getting the multiplying factor for 30.1 atmospheres leaves little uncertainty as to its accuracy. In the same way the multiplying factor of the same electroscope at 9.26 atmospheres was found to be 6.22.

V. Significance of Pressure-Ionization Relations

Bowen and I[3] have already pointed out that the significance of the foregoing pressure-ionization relations is simply that it is impossible to obtain saturation at high pressures. In the case of gamma-rays the immediate ionizing agent is a beta-ray and on the average the detached electrons are not thrown far away from the parent atom. When the pressure is increased thirtyfold this distance is greatly reduced and the powerful recombining forces cannot be entirely overcome by any ordinary increase in field strength. Indeed, changes in applied potential from one hundred to three hundred volts are found to cause at 30 atmospheres no appreciable increase in current, i.e., the currents appear saturated though in fact less than half the electrons actually detached are caught.

That the foregoing is the correct explanation of the pressure-ionization relations can be seen from the following considerations. The ionization produced within an electroscope by gamma-rays is always a little higher than that computed for free air by means of the so called Eve number because there is a small positive wall-effect. Now the mass absorption law is found to hold quite accurately for atoms of nearly the same atomic weight. When, therefore, the absorbing mass inside the electroscope is increased by crowding in say thirty times as many of the same molecules as are already there the absorption *must* be increased in the same proportion, and the absorption must manifest itself in the ions formed. If, then, we find by experiment that we get only half the expected number of ions it can only mean that we have not caught them all. That the cosmic rays behave in this respect just as do the

[3] Millikan and Bowen, Nature **128,** 582, (1931).

[4] This result was also found by Hoffmann, Zeits. f. Physik **69,** 704 (1931). See also Hoffmann and Lindholm, Gerlands Beiträge zur Geophysik **22,** 23 (1928).

gamma-rays must mean that in the case of cosmic rays the immediate ionizing agent is either a negative or a positive electron or both, for the general type of ionization is the same for electrons and for protons, as the Wilson tracks show.

VI. Cosmic-Ray Ionization at Sea Level

The result found above that the cosmic-ray ionization at Pasadena in Electroscope No. 3 is 2.63 cc/sec. is somewhat surprising because it is larger than our preceding estimate. Its accuracy, however, is very much greater than that obtained in any of our preceding work done with electroscopes at a pressure of one atmosphere, for the foregoing multiplying factor 13.80 is known with great certainty as the above data show, and the ionization at Pasadena taken from the Millikan-Cameron-30-atmosphere curve is a weighted mean of many observations, and its value is accurately 37.5 ions cc/sec. Now $(37.5-1.2)\div 13.80$ gives exactly 2.63, which is the ionization at Pasadena at 24° C, 74 cm pressure, the conditions at the time of filling the electroscope and in terms of which the pressure of 30.1 atmospheres was computed. As can be seen from the ionization-depth curve, 2.63 ions cc/sec. at Pasadena corresponds at sea level, i.e., at 10.33 meters of water, to 2.48 ions cc/sec. in place of the 1.4 or 1.6 ions cc/sec., which was published as a result of our early under-water work done in 1925 and 1926 before the technic of accurate cosmic-ray measurements had been developed.

The other two electroscopes here used, No. 1 and No. 2, when worked out in the same way give results in fair agreement, No. 1 giving cosmic-ray ions at Pasadena 5 percent lower than No. 3 and No 2 giving a value 7 percent higher. But the results with No. 3 are by far the most dependable. Not only the ionization-depth curve itself but the constants derived from it are so much more accurate than any of our previous results obtained with the earlier and much less sensitive electroscopes that although I can find no disagreements between the previous work and this that lie outside the older experimental uncertainties, this newer work should entirely replace the older at points at which they overlap. These former experimental uncertainties lay partly in the measurements of the electrical capacities of the fibers, then only roughly determined, but especially in the zeros of the electroscopes, insufficient depths and insufficient sensitivities having been used in determining them in the earlier work. This earlier work, too, was done with entirely different electroscopes which need not have the same wall-effects as has No. 3 here used, though I do not think this should make so large a difference. It is true that all measurements of the absolute value of the cosmic-ray ionization at sea level relate to the particular electroscope used and in general contain an unknown wall-effect. This effect, however, is probably rather small so that it is now highly probable that the absolute value of the cosmic-ray ionization in open air at Pasadena is somewhat over 2 ions. I hope to report later on the reduction of the values here found for electroscope No. 3 to absolute values in free air.

ON AN ATTEMPT TO DEFLECT MAGNETICALLY THE COSMIC-RAY CORPUSCLES

By L. M. Mott-Smith
The Rice Institute

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Abstract

This paper reports the results of an experimental attempt magnetically to deviate the high-energy corpuscles associated with the cosmic radiation. With a magnetic analyser involving the use of Geiger-Müller electron counters and the magnetic field in the interior of a magnetized iron bar, it is found that no deviation of the corpuscles which cause the simultaneous discharges of the counters occurs. Calculation of the sensitivity indicates that an observable deviation would have been produced if the corpuscles were electrons of energy 2×10^9 *e*-volts or less or portons of energy 10^9 *e*-volts or less.

The difficulties involved in explaining this result are discussed and various possible interpretations are presented.

Introduction

IN THE present paper will be reported the results which have been obtained in the attempt magnetically to deviate the cosmic corpuscular radiation. The general character of the method has been described,[1] and preliminary results have already been presented.[2] The present experimental method was devised at about the same time independently by Rossi,[3] by Tuve,[4] and by the author. Results were first obtained by Rossi, who found that the greater part of the corpuscles passing through his apparatus if assumed to be electrons had an energy greater than about 10^8 *e*-volts. Recently a note by Rossi[5] has appeared in which he presents new results obtained by a more sensitive method which indicates energies greater than 10^{10} *e*-volts on the above assumption.

The starting point of this work was the work of Bothe and Kolhorster[6] who found that the cosmic radiation seems to consist principally of high energy ionizing particles. At that time it seemed natural to assume the particles to be electrons; and from their penetrating power it appeared that their energy had to be of the order of 10^9 *e*-volts. In order to obtain more definite information with regard to their energy an apparatus was set up which could give measurable deviation of electrons of this energy. Contrary to expectation, however, it turns out that no deflection is observed. It does not

[1] L. M. Mott-Smith, Phys. Rev. **35,** 1125 (1930).
[2] L. M. Mott-Smith, Phys. Rev. **37,** 1001 (1931).
[3] B. Rossi, Rend. Acc. dei Lincei **2,** 478 (1930).
[4] M. A. Tuve, Phys. Rev. **35,** 651 (1930).
[5] B. Rossi, Nature **128,** 300 (1931).
[6] W. Bothe and W. Kolhörster, Zeits. f. Physik **56,** 751 (1929).

seem possible to find a satisfactory interpretation of this result at the present time. However, some interesting questions are raised so that it seems worth while to present the experimental method and the results in detail.

Experimental

Method

The experimental method is based on the discovery by Bothe and Kolhörster that the high-energy particles associated with the cosmic rays can be studied by making use of their ability to cause the simultaneous discharge of two neighboring Geiger-Müller tube electron-counters.[7] This "coincidence method" is a very powerful means of studying these particles since this effect, save for chance coincidences, which can easily be allowed for, is practically entirely due to the cosmic radiation, and because it is possible to detect individual particles.

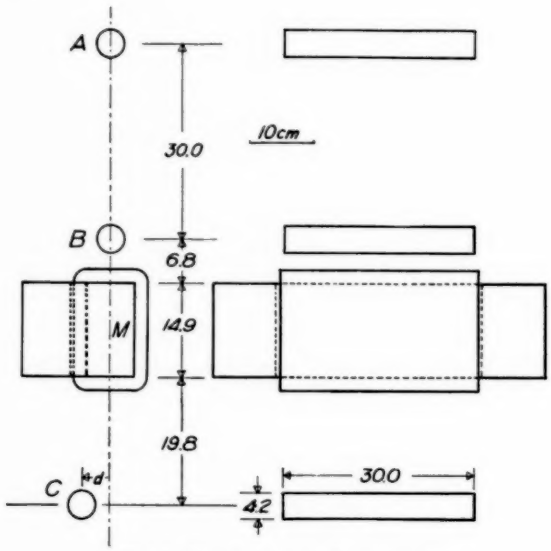

Fig. 1. Arrangement of apparatus.

For the purpose of magnetic analysis of these particles, Bothe and Kolhörster's method of counting coincidences between two counters was extended by the introduction of a third counter and recording the triply coincident discharges of the three. It was verified that the frequency of the triple coincidences under various geometrical arrangements of the three counters was exactly that to be expected on the assumption that the discharges are caused by the rectilinear passage of an ionizing particle through the apparatus, entirely in accord with Bothe and Kolhörster's position with regard to the meaning of the coincident discharges. (Evidence for this comes from the experimental results to be presented below.) The triple coincidence arrangement made it possible to set up a magnetic analyser because it allows a narrow beam of the particles to be picked out of the diffuse radiation by using

[7] H. Geiger and W. Müller, Phys. Zeits. **29**, 839 (1928).

two of the counters as collimators. The two counters are indicated at A and B of Fig. 1, which represents the two vertical elevations of the apparatus. The third counter, C, placed below, serves to explore the beam defined by the first two. It will be evident that if only triply coincident discharges of the three counters are recorded any particles which reach the analysing counter without passing through both collimating counters are not registered and that consequently the two upper counters act exactly as a pair of slits in rejecting all particles which do not pass through them.

For studying the magnetic deviation of the particles a region of magnetic field is introduced just below the second counter. It was found that with the separation of the counters required to give what was believed to be sufficient resolving power, the length of the tubes had to be relatively great in order to give a counting rate high enough to render the experiment feasible. Since the magnetic field must be directed parallel to the axis of the cylinders and since a reasonably strong field over a path of the order of 10 cm was needed, it was difficult to produce a strong enough field throughout this large volume without very powerful electromagnetic equipment. Accordingly in this experiment the magnetic field in the interior of a block of magnetized iron is employed. That such a scheme would be feasible and convenient for deviating these very penetrating particles was first pointed out by Skobelzyn.[8] The closed core magnet used for this purpose is indicated at M, Fig. 1. In this manner it was possible to obtain a strong enough field so that a measurable deviation of electrons of 10^9 e-volts energy would be expected.

The experiment then consists in exploring the beam by observing the frequency of the coincidences at various displacements, d, of the lowermost counter and looking for a change in position or shape of the intensity maximum as the iron core is magnetized.

Details of apparatus

The Geiger-Müller counters. In as much as it was necessary to take counts continuously over a period of several weeks, it was essential that the G.-M. tubes should maintain constant characteristics during this period of time. Since difficulties might be experienced with leakage or slow changes of the

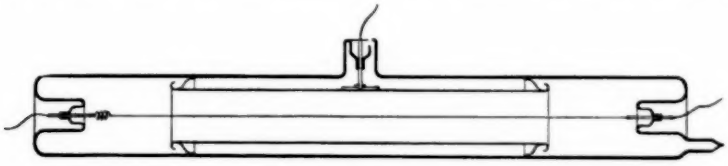

Fig. 2. Detail of Geiger-Müller counter.

gas in tubes not permanently sealed up, the tubes were enclosed in a glass envelope which could be sealed off. The details of construction will be evident from an inspection of Fig. 2. The tube is formed from sheet copper, with the usual "can" joint. Its ends were flared over to prevent strong electric fields at

[8] D. Skobelzyn, Zeits. f. Physik **54,** 686 (1929).

the sharp ends. The tube is supported in the Nonex glass container partly by two spring skirts bearing against the glass and partly by the side lead. The central wire is of tungsten 0.076 mm in diameter, supported from two tungsten seals one at each end of the envelope. A tungsten spring holds the wire taut. To prepare the tubes for operation they were baked out at about 350°C for several hours on the pumps in accordance with the usual high-vacuum technique. The central wire was then cleaned by electrical heating to incandescence for a few moments. After this treatment the tubes were allowed to cool, the pumps were shut off, and finally air was slowly introduced, passing through a liquid-air trap for removal of water vapor and radioactive emanations. The pressure chosen was 7.0 cm of mercury. The tubes were finally sealed off and were then ready for use.

A preliminary test of a tube constructed in this manner showed that its counting rate remained practically unaltered during about six weeks of continuous operation. Tests of the individual counting rates of the particular tubes used in the present experiment were not deemed necessary, though from experience with tubes of similar dimensions and construction the number of discharges per minute is estimated to be about 200 at sea level and with normal radioactivity of the surroundings.

The magnet. The "magnet" consists of a closed core of solid mild steel with a magnetizing winding of about 2000 turns on the leg through which the corpuscles passed. Its dimensions are given in Fig. 1. A magnetic induction of 17,000 was obtained with a current of 2.2 amperes. The induction was determined by means of a fluxmeter and single turn coil linking the core.

The coincidence selector and counter. For the present work it was essential to have an entirely automatic device for selecting the triple coincidences out of the single and paired impulses. Besides it was highly desirable to record and sum the triple coincidences automatically. Accordingly, Bothe's[9] automatic method of accomplishing these results for paired coincidences was extended to selecting and counting triple coincidences.[10]

The diagram of connections of the vacuum tube arrangement for selecting and recording the triple coincidences is shown in Fig. 3. The single impulses from the G.-M. tubes A,B,C are separately amplified by the three tubes T_1, T_2, T_3. The function of the interposed blocking condensers and grid leaks is to shorten the duration of the impulse and was shown by Bothe to be necessary if the selector is to give good resolution. The amplified impulses from two of the counters then actuate the grids of a double grid tube, T_4. As Bothe has shown, if the two grids of a double grid tube are maintained at a suitable negative potential with respect to the cathode, then the potential of either grid can be separately raised a considerable amount without causing current to flow in the plate circuit. On the other hand, if both grids are simultaneously raised, current flows in plate circuit. Accordingly, the impulses arriving at the grids of tube T_4 will only give a pulse of current in the output circuit of

[9] W. Bothe, Zeits. f. Physik **59**, 1 (1930).
[10] B. Rossi, Nature **125**, 636 (1930).

this tube when they occur simultaneously, or more precisely, when their overlapping is sufficiently large. The output of this tube is then combined with the single impulses of the third counter by means of a second double grid tube, T_6, which operates in exactly the same manner as T_4. Hence in the output circuit of this tube will only appear impulses due to triply coincident discharges. The tube T_5 is interposed between these two tubes (T_4 and T_6) in order to convert the negative impulse from the output of tube T_5 into a positive one, since it is evident that the operation of the double grid tube as a selector requires impulses which increase the potentials of its grids. The triple coincidence impulses are then amplified by the two stage amplifier T_8, T_9. The amplified impulses operate the relay R_1 and are finally recorded on the impulse counter. It was found, however, that the operation of the impulse counter was considerably improved by the introduction of the delay circuit, comprising the tube T_9 and the second relay, R_2, connected as shown. This circuit was necessary because during the very short time interval that

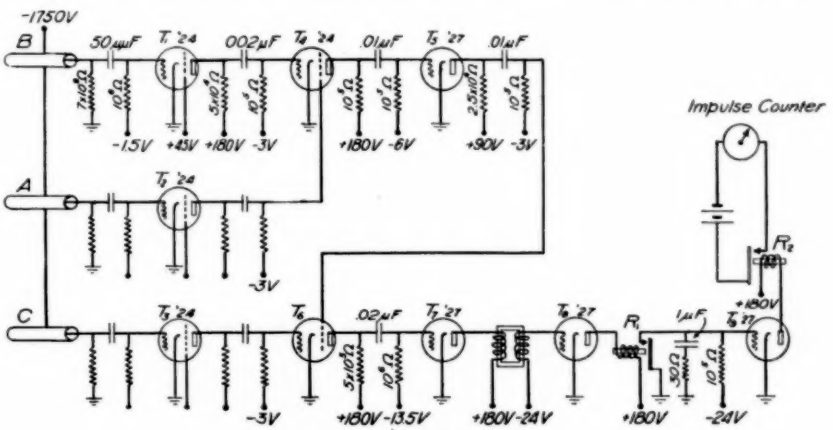

Fig. 3. Diagram of connections.

the relay R_1 remained closed it was not possible to pass sufficient energy to operate reliably the impulse counter.

The various details of the selector and counter, such as the method of coupling between tubes, the values of the plate and grid potentials, etc., will be evident from inspection of the diagram. The final adjustment to proper working condition was principally a matter of trial and error involving the adjustment of the amplification of the various amplifier tubes by altering the coupling resistances, and the setting of the steady grid potentials on the selector tubes. (The values of these quantities indicated on the diagrams are only approximately given for illustration; their correct exact values depend on the characteristics of the G.-M. tubes, the amplifier tubes, etc.) The final adjustment was governed by the criteria that if any one of the G.-M. counters is rendered inoperative no impulses should be registered, and that the triple coincidence counting rate should be the expected value based on the known intensity of the cosmic radiation and the geometry of the arrangement. In its

final adjustment the selector gave no counts for a period of one hour when any one of the three counters was rendered inoperative by earthing the cylinder, under conditions when a count of about 30 impulses per hour would have been obtained if all three counters were operating. In addition, tests were made on the counting rate as the lower or central counter was moved out of alignment and in each case the counting rate was reduced to a small fraction (about 10 percent) of the rate with the three counters in alignment. It should be pointed out that no direct tests could be made to determine whether all the triple coincidences were being registered. In fact with all electrical coincidence selectors this doubt seems to be present. However, from the consistency of the results with various adjustments of the amplifier it is believed that an inappreciable fraction is lost, but in any case this question is of little importance for the present experiment since we are principally interested in the relative values of the counting rate under various experimental conditions.

Procedure and results

The investigation of the effect of the magnetic field consisted in two principal series of runs each extending over a period of six to eight weeks, during which time the apparatus was maintained in continuous operation. Between

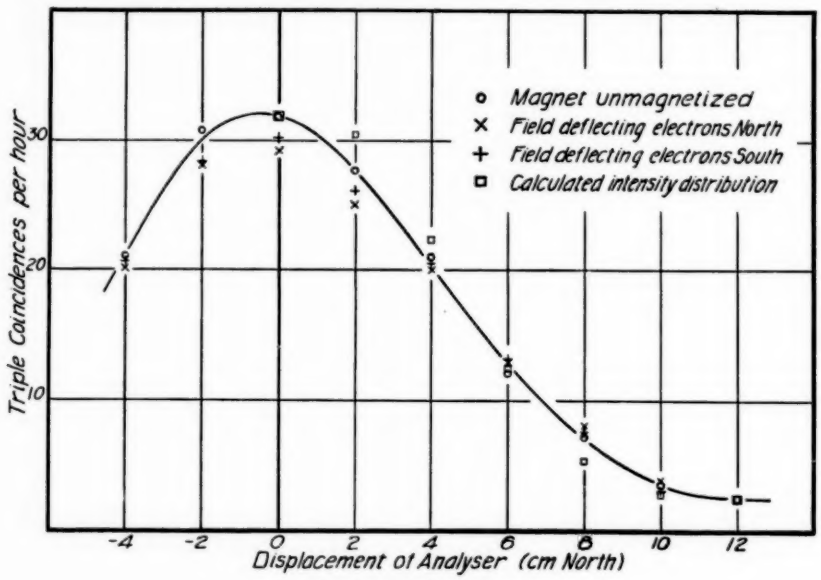

Fig. 4. Principal Data.

the two series the vacuum-tube rectifier which furnished the potential for the counters was replaced by a dry-cell battery because it was suspected that some fluctuation in counting rate was caused by unsteadiness of this potential. However, no evidence could be found showing that improvement in accuracy resulted from this change and accordingly the results from both series are averaged together. The individual determinations at each setting of the

analysing counter and under various conditions of magnetization of the magnet usually were of about twelve to twenty-four hours duration, though in some cases runs lasting as long as forty-eight hours were made. During the course of the experiment the counts at the central position with the magnet unmagnetized as a standard condition were frequently repeated to test for possible secular changes in the counters or in the electrical system. No evidence of such effects was found.

The data are graphically represented in Fig. 4. The points in this figure are the averages of usually numerous separate runs at each of the various settings. These averages were of course taken by summing the total number of coincidences at each setting and dividing by the total time interval. The probable error of the individual points is estimated to be about 3 percent. In making this estimate it has been found necessary to take account of both the statistical error due to the random arrival of the corpuscles and of certain other sources of fluctuation also of a more or less random nature whose cause is not exactly understood but whose magnitude could be estimated by suitable statistical treatment of the separate runs at a particular setting. To indicate the method of estimating the probable error, and as a sample set of data, the results of the separate determinations at the central position with the magnetic field on, deflecting electrons north, are given in Table I. The number of separate counts for this position is not as large as that for certain other

TABLE I. *Sample of data*

Interval (hours)	Count (C)	Rate C/hour	Deviation (D)	CD^2	
19.32	588	31.5	2.1	2600	Average rate $=\frac{4454}{151.5}=29.4\ C/\text{hr}$
17.79	494	27.8	−1.6	1300	Standard deviation $=\frac{(8400)^{1/2}}{4454}=1.4$
14.40	451	31.3	1.9	1600	Probable error $=0.67\times1.4=0.92$
12.00	360	30.0	0.6	100	$\%$ P.E. $=\frac{0.92\times100}{29.4}=3.1$
24.13	690	28.6	−0.8	400	Statistical error $=0.67(4454)^{1/2}=0.29$
39.90	1134	28.4	−1.0	1100	$\%$ S.E. $=\frac{0.29\times100}{29.4}=1.0$
24.00	737	30.7	1.3	1300	
151.54	4454			8400	

points but somewhat greater than that at a few others, so that it may be taken as an average sample. Taking the separate runs as individual observations, the probable error has been computed by the usual method. In making this calculation, since the counts are not all of the same number, the observations have been given weights proportional to the number of coincidences counted. As indicated in the table, the probable error for this set of counts is 3.1 percent and is taken to be the true probable error of the quantity in question. It will be noted that the statistical error is considerably smaller; only

1 percent in this case. Similar treatment of the rest of the data yields approximately this same figure or better. For example, the figures for the numerous runs at the central position, magnet unmagnetized, are: probable error computed in the above manner, 2.9 percent; statistical error, 0.7 percent.

The points at 10 and 12 cm north represent the count due to coincidences occurring by chance, because at the 10 cm position the analyser is just outside of the geometrical limits of the beam. The fact that the count at 12 cm is nearly the same as that at 10 cm indicates that there is very little scattering of the corpuscles in passing through the magnet.

On this figure have also been indicated the values of the counting rate which are expected assuming that the corpuscles pass rectilinearly through the apparatus, and that the entire cross-sectional area of each counter is effective. In calculating this curve the experimentally observed counting rate at the central position and the "chance" count for the point at 10 cm have been

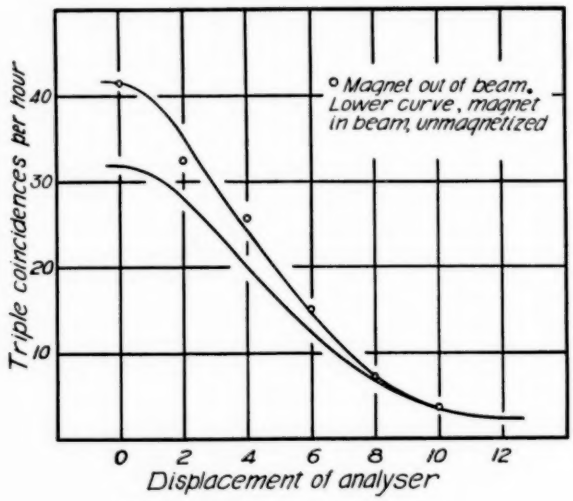

Fig. 5. Absorption due to magnet.

taken as given and the other points then computed. It will be noted that the calculated shape of the intensity maximum is slightly different from the observed. However, this difference is undoubtedly due to trivial causes such as inaccuracy in alignment and construction of the counters or lack of sensitivity of the counters for a corpuscle passing through very near the cylinder. It may be said that on the whole the experimentally observed intensity maximum is of the character to be expected under the above assumption.

A subsidiary set of runs was also made with the magnet removed from the beam for the purpose of observing the absorption due to the magnet as well as a possible widening of the beam due to the scattering of the radiation by the iron. The curve obtained for this condition is presented in Fig. 5. Only very rough determinations were made of the various points, with exception of that at the central position whose accuracy is as high as the data presented above. The curve for the magnet in position but unmagnetized has been re-

peated on this figure for purpose of comparison. One feature of interest in this determination is that we can obtain from it a check on the observation of Bothe and Kolhörster[6] and others that the absorption coefficient for the corpuscles responsible for the coincidences is nearly the same as the appropriate cosmic-ray coefficient determined by the electroscope measurements. The amount of absorption in passing through the magnet can be obtained from the two ordinates at the central position (41.5 and 31.8). Allowing for the chance count (3.0), we obtain, $I/I_0=0.75$. The expected change can be obtained from the water-equivalent thickness of the magnet and Millikan and Cameron's[11] cosmic-ray intensity curve. Assuming the mass law, the water equivalent of the magnet (15.1 cm of iron and 2.0 cm of copper) is 136 cm. From the curve we find, taking the ionization at 10.5 meters and at 11.9 meters, $I/I_0=0.81$, in good agreement with the observed value. The discrepancy is in the right direction to be explained by a failure of the mass law such as has been found by Millikan and Cameron[11] for their lead electroscope shield. It is also of interest to note that there appears to be little or no scattering of the radiation by the iron. If the part of the radiation (amounting to 25 percent) which is lost from the incident beam is removed mainly by scattering at small angles we should expect to find an appreciable broadening of the beam when the magnet is in position. It seems therefore that the corpuscles must be either absorbed or scattered at large angles. Though it would seem that interesting information with regard to the character of the radiation could be obtained by analysis of this observation it has not seemed worth while to attempt this until more accurate data on the scattering have been obtained.

Returning now to a consideration of the data of Fig. 4 it will be noticed that the values obtained when the magnetic field is present lie somewhat below those for no magnetization but that no significant shift or broadening of the intensity maximum on magnetization is observed. In the results which were previously reported, a similar lowering was observed but on account of the uncertainty of the measurements it could not be concluded that the presence of the magnetic field had any effect whatever on the shape of the curve. In the case of the present results it is probable that the observed lowering of the curve is significant. This effect is undoubtedly due to the presence of relatively low energy secondary particles. Such particles accompanying the cosmic radiation have been observed by Geiger.[12]

But what is perhaps of greater interest is that no significant displacement of the maxima for the two directions of magnetization is observed. To discuss the meaning of this result it is necessary to calculate the sensitivity of the apparatus. We first obtain the deviation experienced by an electron passing axially down through the apparatus. In making this calculation the force on the electron while in the interior of the magnetized iron is taken to be $e/c\,[v\times B]$, where e, v and c have their usual significance and B is the magnetic

[11] R. A. Millikan and G. H. Cameron, Phys. Rev. **37**, 235 (1931).
[12] H. Geiger, Proc. Roy. Soc. **A128**, 331 (1931).

induction. A few words in justification of this procedure may not be out of place. On the electromagnetic theory the induction represents the average value of the actual internal magnetic field. It is hardly conceivable that this average is made up of values so distributed that a majority of the electrons are able to pass through the iron without passing through the region where the field is large. Accordingly it seems that unless our notions of the nature of magnetic bodies are quite incorrect the above relation for calculating the deflection must give correct results, at least to a first approximation. For electrons whose velocity is so great that their moving mass is large in comparison to their proper mass, as will be true in the present case, the expression for $H\rho$ reduces to the simple form, $H\rho = 3.3 \times 10^{-3} V$, where ρ is the radius of curvature of the path in a field of strength H, and V the energy of the electron in equivalent volts. Putting in the value of H, 17,000 gauss, we obtain $\rho = 1.9 \times 10^{-7} V$. The deviation at the analysing counter produced by this curvature of the path is readily computed to be, $d = 420/\rho$.

It may first be assumed that all the electrons are arriving with the same velocity, in order to find a lower limit for this quantity. In this case, to a good approximation, the entire intensity maximum will be shifted to one side an amount equal to the calculated deviation for an axial electron. Although it is somewhat difficult to arrive at an exact estimate of how large a shift could have been observed, an inspection of the curve of Fig. 4 and the probable uncertainty in the points indicates that a displacement of 1 cm could not have escaped notice. (It should be remembered that the separation of the maxima for the two opposite senses of magnetization will of course be twice the calculated value). Introducing the value 1.0 cm it is found that the permissible ρ is 420 cm and the equivalent voltage $420/1.9 \times 10^{-7}$, or approximately 2×10^9 volts. A similar computation for protons indicates that if the particles are protons their energy must be greater than about 10^9 e-volts.

Discussion

If the radiation is indeed composed of electrons (or protons) a surprising feature of the present result is the apparent entire absence of deflectable ones, because on present ideas it would be expected that a considerable fraction of the radiation should consist of relatively low speed electrons. If nuclear effects are negligible, as has been always supposed when dealing with the absorption of high energy particles, it would seem that the principal causes of removal of electrons from the beam will be (1) complete loss of energy by production of ionization along the path and (2) by multiple scattering. When dealing with electrons whose energy is 1000 times that of an α-particle and whose momentum is of the same order it is evident that multiple scattering becomes a negligible factor in this process.[13] The principal factor in producing the absorption must be the loss of energy along a rectilinear path. Now the cosmic radiation is know to follow an approximate exponential law of absorption. In order to obtain such a law with this process of absorption it is

[13] See also calculations on the multiple scattering in the article of reference 6.

necessary to make the *ad hoc* assumption of an exponential distribution in number of electrons of given initial velocity. In addition it must be expected that a considerable fraction of the electrons composing the beam should have relatively low energy. This is readily seen without detailed calculation by the following consideration. It may be found, for example, from Millikan and Cameron's curve that 30 percent of the electrons passing through the magnet are destined to be absorbed in the next 2.5 meters water equivalent of absorbing material. The ionization along the path amounts to, say, 40 ion pairs per cm in air at atmospheric pressure, or 3×10^4 ions per cm of path in water, and 30 *e*-volts energy is lost on the average at each ionization. Hence the initial energy of the fastest of this fraction of the particles must be $30\times3\times10^4\times250$ or 2×10^8 *e*-volts. Were this the case a large magnetic effect would have been observed, since electrons of this energy or less would have been completely removed from the beam. A calculation based on these assumptions indicates that in order to account for the present result the loss of energy per cm of path must be of the order of 100 times greater than the above, and the initial energies correspondingly 100 times higher. This means that these electrons would have to produce at least 10,000 ions per cm of path. Though on latest theoretical ideas[14] the ionization along the path is found to increase as the energy of the electron becomes high, direct experimental evidence from the work of Skobelzyn[15] and of Mott-Smith and Locher[16] seems to show that the ionization due to cosmic corpuscles is only of the order of 30 ion pairs per cm of path. It follows that if the particles are electrons they must be removed from the beam in a manner analogous to that occurring in the case of photons. That is, the electrons must be removed not by a gradual loss of energy but by a single or at the most a few encounters entailing a large loss of energy. Attempts to find a possible process of this sort for electrons have so far failed. In fact it seems impossible to get rid of the enormous quantity of energy by any sort of mechanism. Disregarding possible theoretical difficulties, the most favorable assumption which it seems possible to make is that the electron, on having a sufficiently close encounter with a nucleus, enters it and remains attached, the greater part of its energy going into internal nuclear energy in the process. However, since momentum must be conserved the nucleus recoils with considerable velocity. Consideration of this process indicates that it would satisfy the requirements of the present experiment and not be in obvious contradiction with other experimental facts, though perhaps difficult to account for theoretically. (For example, the fraction of atoms altered by the capture of cosmic electrons is negligibly small during a period of, say, 10^9 years). However, a consequence of these ideas is that the bulk of the ionization due to cosmic radiation must be directly due to the recoil nuclei. Furthermore, the passage of such a nucleus through an electroscope will be relatively infrequent, so that it is required that the ionization should be observed to oc-

[14] J. F. Carlson and J. R. Oppenheimer, Phys. Rev. **38,** 1787 (1931).

[15] See reference 8.

[16] L. M. Mott-Smith and G. L. Locher, Phys. Rev. **38,** 1399 (1931).

cur in relatively large and observable spurts. This effect apparently has not been observed by any of the electroscope workers though it seeems that had it been present it could not have escaped notice. In addition a special test for this effect has been made here, by using a high pressure ionization chamber and short period electrometer, with negative result, so that this possibility has to be abandoned.

Accordingly it seems difficult to believe that the corpuscles responsible for the coincidences are electrons or protons unless the effective magnetic field in the iron is of a different order of magnitude than the value of the induction. And if this is the case, it means very drastic changes will be needed in theories of magnetization. It would be very desirable to test this possibility by repeating this experiment with an ordinary "air" magnetic field. However, very powerful electromagnetic equipment would be required to obtain the necessary sensitivity. (On account of the observed penetrating power, these particles must have energies of at least 10^8 *e*-volts.)

If the coincidences were caused by the passage of a photon through the counters, the present results are at once explained. However, on both theoretical grounds and by direct experimental evidence this possibility seems to be excluded. On the theoretical side it has been shown by Bothe and Kolhörster that photons cannot produce the coincidence effects. On the experimental side it has recently been shown by Mott-Smith and Locher[16] that the corpuscle which causes the coincidence makes an ion-track in the cloud-chamber, a fact which seems definitely to exclude the possibility that the corpuscle is a photon.

Another possible explanation is one which has been recently advanced by Pauli[17], and by Carlson and Oppenheimer[14], that these cosmic corpuscles are neutrons. In this case attempts to deviate them magnetically are necessarily futile. Evidence in favor of neutrons comes also from the calculations of Carlson and Oppenheimer on the relative ionizing power of electrons and neutrons. They find that while the ionization (number of ions per cm of path) by electrons of energies required to account for cosmic ray phenomena should be somewhat higher than that observed in cloud tracks of these particles by Mott-Smith and Locher, that of neutrons may be of the right order of magnitude. Though this possibility is in many ways attractive, it seems that evidence of a more direct nature will have to be found for the existence of neutrons before it can seriously be concluded that the cosmic-ray phenomena are due to them.

[17] W. Pauli, Presented in a speech at the meeting of the A.A.A.S., June 16, 1931.

PERTURBED SERIES IN LINE SPECTRA

By A. G. Shenstone and H. N. Russell
Princeton University

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Abstract

There occur many line series in atomic spectra which do not even approximately fit a Ritz formula. They display either a sudden rise in the value of n^*-n towards high term values or a gradual fall of almost a unit. The latter type contains an extra term due to some other structure and becomes similar to the first type after the removal of that term. It is shown that all such series obey approximately a series formula of type $\nu_n = R/n^{*2}$, $n^* = \mu + \alpha\nu_n + (\beta/\nu_n - \nu_0)$ in which ν_0 is the wave number of some level of the same type from a different electron structure. The series in the spectra Ca I, Ba I, Hg I, Cu I, Al II are discussed in detail. The rules governing the occurrence of a perturbation are more restricted than the simple ones that can be deduced from the results in other perturbation problems. The constant β is always negative and the trems therefore appear to repel each other. The Ba I levels $5d6p\ ^{3\&1}P^0D^0F^0$ and the series $6snf\,^1F^0$ are given for the first time.

IN A letter to the Editor of the Physical Review[1] R.M. Langer has described a generalized form of the Rydberg-Ritz series formula, deduced from the perturbation theory of the wave mechanics. In the case of atoms containing more than one optical electron, the series formula is given by

$$\nu_n = \frac{R}{\left\{n + \sum \frac{p_{in}}{\nu_n - \nu_1}\right\}^2}$$

in which ν is the term value expressed in wave numbers. Normally this form reduces to a Ritz formula

$$\nu_n = \frac{R}{(n + \mu + \alpha\nu_n)^2}.$$

Cases arise, however, where the atom has states of nearly equivalent energies arising from different electron configurations, and the mutual perturbations must then be considered. Langer does not state the conditions necessary for the perturbations to occur, but one can deduce them with some degree of certainty from the results of similar calculations, for predissociation, auto-ionization, and band spectrum perturbations.

Perturbations will occur, in general, between terms having the same J-value and parity. In the special case of Russell-Saunders coupling, one must also add that they must have the same L and S values. Actually, this more restricted case is the one most frequently met with.

The object of this paper is to show how Langer's formula explains the

[1] R. M. Langer, Phys. Rev. **35**, 649 (1930).

anomalies which exist in a great many well-known series. It is found that the formula is inadequate to cover all the details, but its success is much beyond the expectations for a first approximation formula.

The type of perturbation most frequently met with occurs when a single term from some more complicated structure falls among the terms of a simple series. In that case, there is superimposed on the ordinary Ritz form, a quantity such as one meets in the formulae of anomalous dispersion, and we have

$$\nu_n = \frac{R}{n^{*2}} = \frac{R}{\{n + \mu + \alpha\nu_n + (\beta/\nu_n - \nu_0)\}^2}$$

in which ν_0 is the value of the foreign level.

The exhibition of term sequences is best accomplished by plotting $n^* - n$ against ν_n. The Rydberg formula is then represented by a straight line parallel to the ν axis, and the Ritz formula by a straight line of slope α and intercept μ. In fact, the best way to find the correct limit of an unperturbed series is to find the condition under which the plot is, as nearly as possible, a straight line.

The sensitivity of this method is very great if the lines involving the high series members are accurately measured. It should be remembered that the values of a set of terms are fixed by the lines, except for an additive constant. If we differentiate n^* with respect to ν_n, we obtain $dn^*/d\nu_n = -\frac{1}{2}(R)^{1/2}/\nu_n^{3/2}$, so that a constant change in the values of all the terms effects the n^*'s of the high terms very much more than those of the low terms. For instance, a change of 1 unit in the values of the terms changes n^* by 0.005 for a term at 1000 and by only 0.000005 for a term at 100,000. Practically, that means that, if a wrong limit is assumed, the end of the plot of $n^* - n$ against ν_n will show a deviation from a straight line of increasing amount as we proceed to smaller term values. If the series is strictly Ritzian, it is possible to make that last portion perfectly straight. In practice, one finds always that the high series members are known with insufficient accuracy, and the best one can do is to use the highest members which are based on accurate measurements. A case in point is the long ^3S series of Hg I in which no manipulation of the limit can even approximately straighten out the series tail. A series of three terms can, of course, always be fitted to a Ritz formula. In this case also the easiest method is trial and error to make the following relation true,

$$\frac{\nu_1 - \nu_2}{\nu_2 - \nu_3} = \frac{(n_1^* - n_1) - (n_2^* - n_2)}{(n_2^* - n_2) - (n_3^* - n_3)}.$$

This follows directly from the formula

$$n^* = n + \mu + \alpha\nu_n.$$

If the method of plotting which has been described is used for a series which obeys strictly Langer's formula, the curve obtained is a hyperbola having asymptotes $\nu = \nu_0$ and $n^* - n = \mu + \alpha\nu_n$. Such a curve is readily recognizable, and is very commonly found. The constants of the formula may be found very easily by the following method.

We first plot $(n^*-n)\ (\nu_n-\nu_0)=\beta+\mu'(\nu_n-\nu_0)+\alpha'(\nu_n-\nu_0)^2$. β is then found from the point where the parabola crosses the line $\nu=\nu_0$. Finally, we plot for each term the quantity $(n^*-n)-\beta/\nu_n-\nu_0=\mu+\alpha\nu_n$ and the remaining constants, μ and α are the intercept and slope of the straight line which represents the plotted points most nearly. In most cases the series fit into such a formula with reasonable accuracy; the greatest deviations being usually near the perturbation and in the first term of the series. The latter lack of agreement is quite usual in unperturbed series also.

In the quantum mechanics the existence of a perturbation implies at least a partial mutual sharing of identities by the terms involved. Such sharing may even become so great that it is impossible to tell which is the perturbing term. The perturbing term may show very nearly the same combining qualities as the series term, and be absorbed into the series as an extra member.

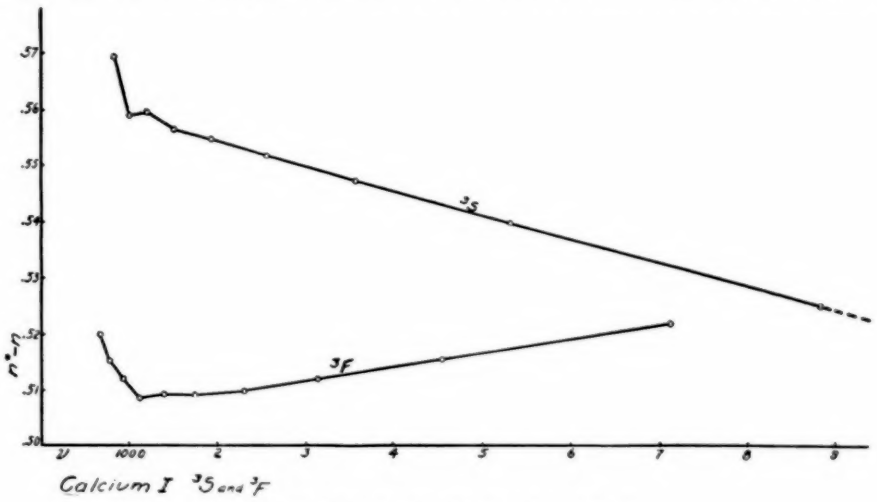

Fig. 1. Plot of ^3S and $^3F^0$ series of Ca I.

Many such cases can be found in the literature of spectra. The resulting plot of n^*-n shows at some point in the series a rather rapid fall of almost a unit. The perturbing term must lie somewhere in the middle of the drop, and its removal displaces vertically upwards the whole curve below its position by a unit, producing the usual hyperbola. This phenomenon occurs in the ^3F series of A1 II, which Schroedinger[2] endeavoured to explain by assigning two terms to the same total quantum number.

There is a surprising number of well-known spectra which contain perturbed series, and some spectra in which almost every series is more or less influenced by a foreign term. The following spectra will be considered in some detail; Ca I, Ba I, Hg I, Al II, Cu I.

Ca I

Before dealing with the perturbed series it is necessary to find as accurate as possible a limit for the whole term system. This must be obtained in Ca I

[2] Schroedinger, Ann. d. Physik **77**, 43 (1925).

from the ^3S and $^3F^0$ series. The ends of both series deviate considerably from a straight line, but the chief portions are certainly most consistent if we retain the limit used by Fowler.[3] The plot of these two series is shown in Fig. 1.

The ^3D sequence is the familiar series in which the intervals at first decrease, then increase to a maximum, and finally fall off to unobservable quantities. The plot of n^*-n shows the characteristic rapid fall of almost a unit, with the term of maximum interval in the middle of the fall. The removal of

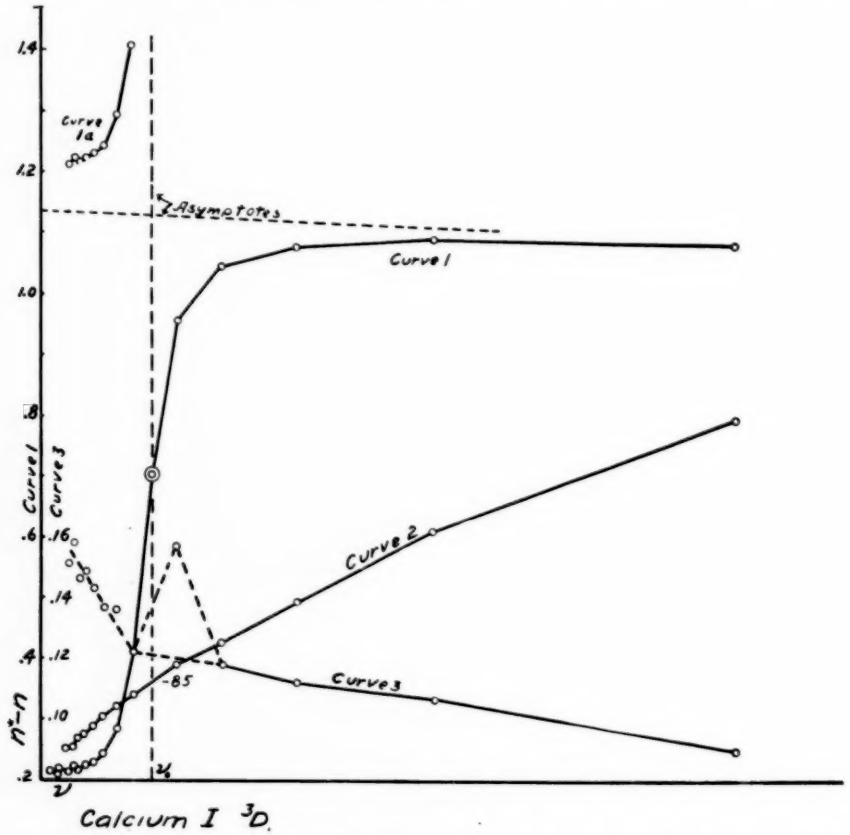

Fig. 2. $^3D_1$ of Ca I. Abscissae $=\nu_n$. Ordinates: Curve 1 n^*-n as the series is usually given. Curve 1(a) n^*-n after removal of perturbing level. Curve 2 (n^*-n) $(\nu_n-\nu_0)$ (No scale shown). Curve 3 $(n^*-n)-(\beta/\nu_n-\nu_0)$. (Scale 5 times scale for curve 1.)

that term from the series leaves the typical hyperbolic curve. It remains to identify the origin of the surplus term and to calculate the series formula. The identity is not difficult to discover, since the term must be of even ^3D nature. It is in the correct position for a structure of very probable occurrence, $3d5s\,^3D$. The assumption of such an origin makes the energy differences $3d5s-3d4d$ and $4s5s-4s4d$ almost exactly equal, as they should be. Additional evidence is given by the following consideration. The two terms $3d4s\,^3D$ and $3d5s\,^3D$ can be considered as successive terms of a series whose limit is $3d^2D$ of

[3] Fowler, Report on Series in Line Spectra (1922).

Ca II. On that basis, the two terms have Rydberg denominators of 1.604 and 2.640, which are very reasonable values. The third term of the series should be at about -5500, but should not be found because of the effect of autoionization.[4]

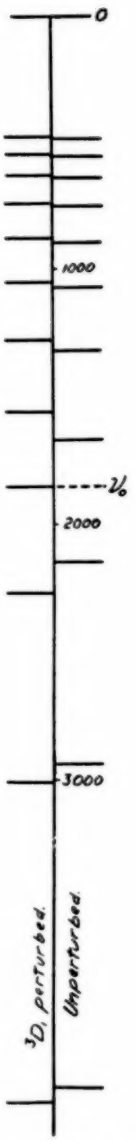

Fig. 3. Energy levels of $^3D_1$ Ca I, as usually given and after removal of the perturbation.

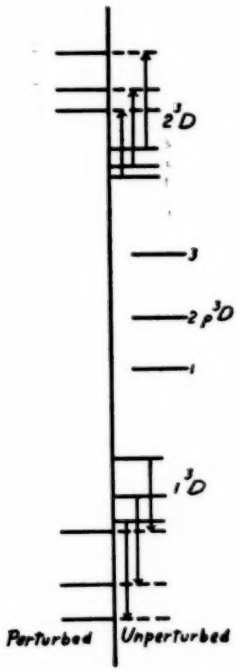

Fig. 4. To show change in term intervals in a perturbed series.

The complete calculations and curves for the $^3D_1$ series are given below. For the remaining series there are given only the series formula, the origin of

[4] A. G. Shenstone, Phys. Rev. **38,** 873 (1931).

TABLE I. *Calculations for series formula to represent the $4snd^3D_1$ series of Ca I.*

1	2	3	4	5	6	7	8	9	10	11	12
28969.1	27120.2	1.9463	−0.0537	−1456.4	−0.0031	−0.0506	−0.0982	0.0476	∽2.0258	∽26465	∽+2504
11556.4	9707.5	3.0815	+0.0815	+791.2	−0.0088	+0.0903	−0.0392	0.1295	3.0815	11556	0
6561.4	4712.5	4.0896	+0.0896	422.2	−0.0180	0.1076	−0.0222	0.1298	4.0893	6562	−1
4255.5	2406.6	5.0780	+0.0780	187.7	−0.0353	0.1133	−0.0144	0.1277	5.0798	4252	+3
3002.4	1153.5	6.0456	+0.0456	+52.6	−0.0737	0.1193	−0.0102	0.1295	6.0456	3002	0
2268.3	419.4	6.9552	−0.0448	−18.8	−0.2026	0.1578	−0.0077	0.1655	6.9260	2287	−19
(1848.9)	0										
1551.3	−297.6	8.4105	+0.4105	−122.2	+0.2856	0.1249	−0.0053	0.1302	8.4105	1551	0
1273.1	−575.8	9.2840	+0.2840	−163.5	+0.1476	0.1364	−0.0043	0.1407	9.2728	1276	−3
1045.6	−803.3	10.2445	+0.2445	−196.4	+0.1058	0.1387	−0.0035	0.1422	10.2318	1048	−2
869.8	−979.1	11.2323	+0.2323	−227.4	+0.0868	0.1455	−0.0029	0.1484	11.2134	873	−3
734.0	−1114.9	12.2273	+0.2273	−253.4	+0.0762	0.1510	−0.0025	0.1535	12.2033	737	−3
628.0	−1220.9	13.2190	+0.2190	−267.3	+0.0696	0.1494	−0.0021	0.1515	13.1970	630	−2
542.2	−1306.7	14.2265	+0.2265	−296.0	+0.0650	0.1615	−0.0018	0.1633	14.1927	545	−3
473.9	−1375.0	15.2172	+0.2172	−298.6	+0.0618	0.1554	−0.0016	0.1570	15.1897	476	−2

Column (1) Term value ν_n; (2) $\nu_n-\nu_0$; (3) n^*; (4) n^*-n; (5) $(n^*-n)(\nu_n-\nu_0)$; (6) $(-85/\nu_n-\nu_0)$; (7) $n^*-n-(-85/\nu_n-\nu_0)$; (8) $\alpha\nu_n$; (9) $n^*-n-(-85/\nu_n-\nu_0)-\alpha\nu_n$; (10) n^*(calc.); (11) ν_n(calc.); (12) ν_n(obs.) $-\nu_n$(calc.).

$4snd^3D_1$

$\nu_n = R/n^{*2}$

$n^* = n+\mu+\alpha\nu_n+(\beta/\nu_n-\nu_0)$

$\mu = -0.8705$

$\alpha = -3.39\times10^{-6}$

$\beta = -85$

$\nu_0 = 1849 = 3d5s^3D_1$

$n = 3, 4, \cdots$

Residuals = ∽+2504, 0, −1, +3, 0, −19, (ν_0), 0, −3, −2, −3, −3, −2, −3, −2

$4snd^3D_2$

$\mu = -0.8678$

$\alpha = -3.571\times10^{-6}$

$\beta = -86$

$\nu_0 = 1839 = 3d5s^3D_2$

$n = 3, 4, \cdots$

Residuals = ∽+2210, 0, +1, +3, 0, −20, (ν_0), 0, −3, −2, −2, −2, −2, −2, −1.

$4snd^3D_3$

$\mu = -0.8656$

$\alpha = -3.665\times10^{-6}$

$\beta = -90$

$\nu_0 = 1829 = 3d5s^3D_3$

$n = 3, 4, \cdots$

Residuals = ∽+2172, 0, +1, +2, −3, −27, (ν_0), −1, −1, −1, −1, −2, −1, −2, −1.

the perturbing term, and the differences between observed and calculated term values.

Fig. 2, curve 1 shows the plot of n^*-n against ν_n, as the series is given in Fowler; and curve Ia after removal of the perturbing term and the consequent addition of a unit to the ordinates of the higher series members. Curve 2 exhibits the values of $(n^*-n)(\nu_n-\nu_0)$ plotted against ν_n, from which the value of β is found at approximately -85, where the curve crosses the abscissa ν_0. Curve 3 is the plot of the remainders on a 5 times greater scale after the subtraction of $\beta/\nu_n-\nu_0$ from n^*-n. This should be a straight line, but shows the same type of deviation in the higher terms as was evident in the supposedly unperturbed ^3S and ^3F series. In addition, one point next to the perturbation shows a rather large deviation. In Table I are shown the various steps in the calculation, and the differences between the observed and calculated terms.

Fig. 3 shows the effect of the perturbation. The energy levels as they are observed and approximately as they would be without the perturbation are shown beside each other to illustrate the magnitude of the effect.

It will be noticed that the constants of the perturbations in the three component series are of about the same magnitude, and that the perturbing term has wider intervals than would normally appear at that position in the series. These two facts explain the anomalous opening out of the intervals in the series terms near the perturbation. The reason for this can best be understood by considering an hypothetical much exaggerated case. (Fig. 4).

The perturbation has the effect of a repulsion proportional to the *nearness* of the perturbed and perturbing levels. The diagram makes it evident that the repulsive effect of the components of p^3D on 2^3D will be greatest for the level of $J=3$ and least for $J=1$. In other words the displacement of $J=3$ will be greater than the displacement of $J=2$ and $J=1$, with the result that 2^3D in its perturbed state will have larger intervals than normal. The same considerations applied to the interaction of p^3D and 1^3D show that 1^3D also will have its intervals increased. If p^3D were an inverted term, we would expect the intervals of 1^3D and 2^3D to be decreased or even inverted. The ^2P series of Cu I is of that type.

^1D *series.*

This series has apparently two perturbations. One is, undoubtedly, due to the level $4p^2\,{}^1D$ at 8585 and the other to a possible level at 1492 which may be either $3d^2\,{}^1D$ or $3d5s\,{}^1D$. The number of members available and the very irregular behaviour makes a calculation unwarranted.

$^3P^\circ$.

There are only three members known in the $^3P_1^\circ$ and $^3P_0^\circ$ series, and four in the $^3P_2^\circ$. The series are perturbed by the known $3d4p\,{}^3P^\circ$ term. The formula has been fitted to the first three members of the $^3P_2^\circ$ series and gives an error of eight units for the fourth member. The constants are as follows:

$$\mu = -1.9489$$

$$\alpha = -7.48 \times 10^{-6}$$

$$\beta = -62.9$$
$$\nu_0 = 9964 = 3d4p\,^3P_2{}^0$$
$$n = 4, 5 \text{ etc.}$$

$^1P^0$.

This series and the equivalent one in Sr I do not yield to the usual methods. There can be no doubt from the evidence of intensities and position that the level 12573 is foreign to the series and originates principally in the structure $3d4p$. The use of that level as ν_0 requires a value of $\beta = -4500$ and the terms deviate from the formula by very large amounts. If we judge entirely from the plot of $n^* - n$, the level at 5372 can be logically removed from the series. The constants of the series are then of reasonable magnitudes and the residuals are quite small. Another possibility is that the second member of the series is actually missing. The formula then requires very large values of α and β. The theoretical elucidation of this series would seem to be of considerable importance.

^1S.

This series is perturbed by $p^2\,{}^1S$ at 8614. The agreement is very poor near the perturbation. The constants are as follows.

$$\mu = -2.3495$$
$$\alpha = -1.066 \times 10^{-6}$$
$$\beta = -100$$
$$\nu_0 = 8614 = p^2{}^1S$$
$$\text{Res.} = \sim +6191, 0, (\nu_0), -245, +2, 0, -1, -1, -1, 0.$$
$$n = 4, 5 \text{ etc.}$$

$^1F^\circ$.

The $^1F^\circ$ series is peculiar in being perturbed by a term $3d4p\,^1F^\circ$ at 8767 which is lower than the first series member. The formula gives a very good agreement with all eight numbers.

$$\mu = -0.0955$$
$$\alpha = 2.93 \times 10^{-5}$$
$$\beta = -80$$
$$\nu_0 = 8767 = 3d4p\,^1F^0$$
$$\text{Res.} = -2, -1, +2, +2, +2, +1, +1, -1.$$
$$n = 4, 5 \text{ etc.}$$

Ba I

The series of Ba I are so irregular that it is impossible to calculate a limit with any certainty; but, from a survey of all the series, it is considered that an improvement can be made by increasing all of the term values given in

Fowler's tables by 3 units. The chief perturbed series is the $6snf\,^3F^\circ$ series (Fig. 5). The perturbation arises from a $^3F^\circ$ term, which is part of a triad $^{3\&1}P^\circ$, D°, F° recently discovered by one of us (H. N. R.) and probably arising

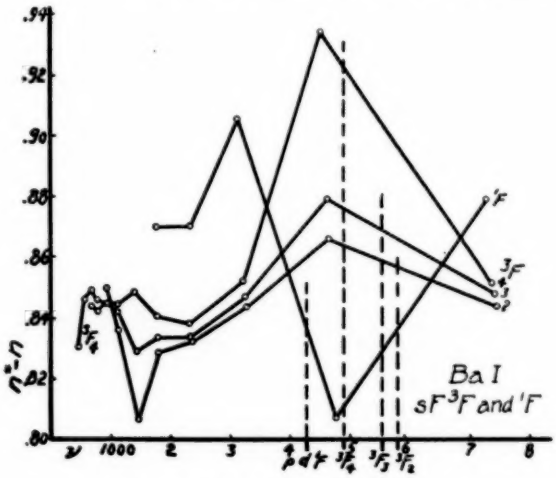

Fig. 5. Plot of ^3F and ^1F series of Ba I.

from $5d7p$. The multiplets are given below in Table II. It will be noticed that two levels, 5039.5 and 3529.9, were previously assigned to the $6snp\,^1P^\circ$ series, The $6snf\,^1F^\circ$ series has also been replaced (H. N. R.) by an entirely new set of terms, which are now found to show a perturbation exactly where expected.

TABLE II. *New multiplets in Ba I. The term values are all measured from* $s^2\,^1S_0$. To obtain value used in this paper, subtract from 42031.4.

	$6s^2\,^1S_0$ 0.00	$6s5d\,^3D_3$ 9596.39	$^3D_2$ 9215.33	$^3D_1$ 9033.87	$^1D_2$ 11395.36
		40 III			
$5d7p\,^3F_4^\circ$ 37131.91		27535.52			
			(4) 15 III		(2u)
$^3F_3^\circ$ 36511.22			27295.84		25115.90
			(2)	(1u) 2 III	
$^3F_2^\circ$ 36235.13			27019.81	27201.18	
		30 III	15 III		
$^3D_3^\circ$ 37540.02		27943.63	28324.72		
		2 III	3 III	10 III	
$^3D_2^\circ$ 37063.18		27466.88	27847.62	28029.46	
	(4) 3 IV		(1u) 3 III	(3) 10 III	(1) 2 III
$^3D_1^\circ$ 36495.65	36495.66		27280.38	27461.78	25100.20
		15 n III	10 III		(2u) 15 III
$^3P_2^\circ$ 37282.08		27685.62	28066.59		25886.64
	(6r) 8 IV		15 III	10 III	(2u) 2 III
$^3P_1^\circ$ 36989.86	36989.82		27774.54	27955.97	25594.55
				10 III	
$^3P_0^\circ$ 36908.21				27874.37	
		(1u)			(5u) 15 III
$^1F_3^\circ$ 37739.96		28142.77 ?			26344.60
			10 III		(2u) 20 III
$^1D_2^\circ$ 37077.44			27861.99		25682.17
	(6r) 8 n IV		3 n III		(3r) 20 NIII
$^1P_1^\circ$ 38499.32	38499.24		29284.20		27103.80

The details of the $^3F^\circ$ and $^1F^\circ$ series are given below. The $^1F^\circ$ series is given in full, since it has not previously been published.

TABLE III. *Constants for $^3F^\circ$ and $^1F^\circ$ series of Ba I.*

Ba

$6snf\,^3F_4$
$\mu = -0.1980$
$\alpha = 8.33 \times 10^{-6}$
$\beta = -33$
$n = 4, 5$
$\nu_0 = 4900.5 = 5d7p\,^3F_4$
Res. = 0, (ν_0), −13, −1, 0, −3, −3, −2, −1, −1, 0, 0, +1

$6snf\,^3F_3$
$\mu = -0.1956$
$\alpha = 8.016 \times 10^{-6}$
$\beta = -32.3$
$n = 4, 5$
$\nu_0 = 5521.2 = 5d7p\,^3F_3$
Res. = 0, (ν_0), 0, 0, +2, 0, +1, −2, −1, 0, 0

$6snf\,^3F_2$
$\mu = -0.1934$
$\alpha = 7.23 \times 10^{-6}$
$\beta = -28$
$n = 4, 5$
$\nu_0 = 5797.3 = 5d7p\,^3F_2$
Res. = 0, (ν_0), 0, 0, +3, +2, +9, 0, −2

$6snf\,^1F_3$
$\mu = -0.1497$
$\alpha = 5.25 \times 10^{-6}$
$\beta = -31.5$
$n = 4, 5$
$\nu_0 = 4292.4 = 5d7p\,^1F_3$
Res. = 0, 0, (ν_0), −9, +7, +5

TABLE IV. $5\,^1D - n\,^1F^\circ$ *series of Ba I.* $5\,^1D = 30637.1$.

λ	*I*	Auth.	ν	*n* ^1F
4283.11	40II	K	23340.9	(4) 7296.2
3861.905	8III	K	25886.6	(5) 4750.5
3636.832	40III	K	27488.7	(6) 3148.4
3531.345	40III	K	28309.8	(7) 2327.3
3463.741	40III	K	28862.3	(8) 1774.8
3921.476	30III	K	29217.8	(9) 1418.3

E & H = Exner and Haschek. K = King.

The F° series are all, undoubtedly, perturbed by the levels given above, but they also show a second possible small disturbance at about $\nu = 1000$. At that position there would be expected the terms arising from the structure $5d4f$.

$^1P^0$.

The $^1P^0$ series of Ba I is given quite incorrectly in Paschen-Götze and in Fowler. One of us (H. N. R.) has recently rearranged the terms of this spectrum and has fixed the following as the $^1P^0$ series.

$$mp\,^1P^0 = 23972, 9485, 6140, 4257, 2724, 2047, 1609 \quad n = 6, 7 \text{ etc.}$$

The series has two perturbations by known terms, $5d6p\,^1P^0$ at 13478 and $5d7p\,^1P^0$ at 3532, but a formula containing two β's can be fitted to it with reasonable accuracy. The constants are as follows:

$$\mu = -3.9192$$
$$\alpha = 4.635 \times 10^{-6}$$
$$\beta_1 = -1179$$
$$\beta_2 = -110$$
$$\nu_{01} = 13478$$
$$\nu_{02} = 3532$$
$$n = 6, 7 \text{ etc.}$$
$$\text{Residuals} = -1380, (\nu_{01}), 0, 0, 0, (\nu_{02}), -6, -30, -5.$$

Hg I

The mercury spectrum contains long series but none of them is capable of giving an accurate limit. The ^3S series is known to the sixteenth member,

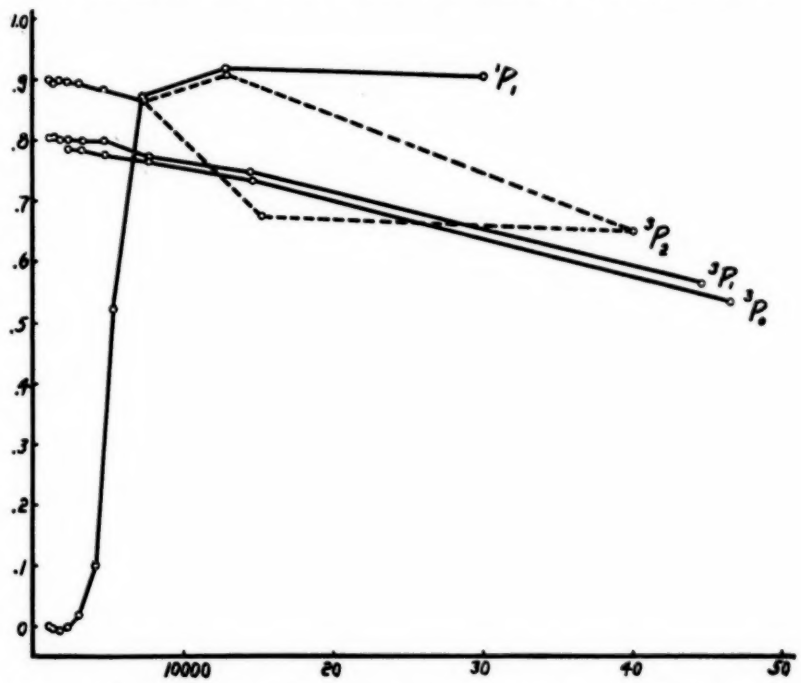

Fig. 6. $^3P^0$ and $^1P^0$ series of Hg I. The second member of $^3P_2{}^0$ may be chosen either way, as indicated in the plot.

but a plot of n^*-n shows a very rapid rise towards the end of the series. The same is true of ^3D. If we accept the usual limit and calculate a Ritz formula for ^3S the residuals are:—

0, 0, +0.5, 0, −0.5, −1.1, −1.7, −0.9, −1.9, −3.5, −3.4, −4.2, −4.3, −3.3.

If we change the limit by +1.5, the agreement is slightly better, except that now the first member is quite far from the calculated position. The residuals are:—

24, 0, 0.2, 0, 0, −0.2, −0.6, −0.4, −1.1, −2.2, −1.9, −2.8, −2.9, −1.7.

For the purpose of the following calculations of the perturbed series, the original limit has been retained, but errors of the magnitude of those above are to be expected. The details of the $^3P^\circ$ series have been taken from a recent paper by Paschen.[5]

The plots of the component $^{3\&1}P^\circ$ series (Fig. 6) indicate that the $^3P_0^\circ$ is unperturbed; that $^3P_1^\circ$ has a small perturbation between the third and fourth members; and that $^3P_2^\circ$ has a large perturbation near the beginning of the series. The origin of the disturbance of the $^3P_2^\circ$ series has been discussed elsewhere.[6] It is attributed to the presence of $5d^9 6s^2 6p\,^3P_2^\circ$, and it has been shown that either the old second member 12974, or the new level 15295, could be attributed to that structure, as far as energy is concerned. It is also true that either one may be taken as a series member and the other as the perturbing level. Both cases have been calculated and can be represented about equally well by a formula. The constant of the perturbation is rather large when the old second member is retained, and we are inclined to believe, therefore, that the other choice is the better. The formulae for both cases are given below. No attempt has been made to include the very low first member.

$\mathrm{HgI}\,^3P_2^0$ (a). $\nu_0 = 15295$

$\mu = -4.0993$

$\alpha = -1.152 \times 10^{-5}$

$\beta = -365$

$n = 6.7$ etc.

Res. $= 0, (\nu_0), 0, 0, 0, +4, +5, +6, +2.$

(b). $\nu_0 = 12974$

$\mu = -4.0842$

$\alpha = -1.129 \times 10^{-5}$

$\beta = -150$

Res. $= 0, 0, (\nu_0), 0, +2, +5, +6, +7, +4.$

In the paper referred to above, it was stated that a possible perturbing term for the series $^3P_1^\circ$ is 7273, calculated from two combinations. That level is, of course, of doubtful reality, but its use does give a very reasonable fit. We are inclined, now, to believe that the perturbation is actually caused by the same level which perturbs the $^1P_1^\circ$ series. Such an assignment is possible because of the fact that the coupling is very far from Russell-Saunders type in Hg I. The perturbation of the $^3P_1^\circ$ series is a very small one, as might be expected in such a case.

$\mathrm{HgI}\,^3P_1^0$ (a). $\nu_0 = 7273? = d^9 s^2 p^3 P_1^0?$

$\mu = -4.1900$

[5] Paschen, Ann. d. Physik **6,** 47 (1930).

[6] Shenstone, Phys. Rev. **38,** 873 (1931).

$$\alpha = -4.15 \times 10^{-6}$$
$$\beta = -3$$
$$n = 6, 7 \text{ etc.}$$
$$\text{Res.} = +2, -1(\nu_0), -10, -1, +1, 0, 0, +1.$$

(b) $\nu_0 = 5368 = d^9s^2p\,{}^1P_1{}^0$
$$\mu = -4.1925$$
$$\alpha = -4.02 \times 10^{-6}$$
$$\beta = -6$$
$$\text{Res.} = -8, +8, (\nu_0), +2, -1, 0, 0, 0, 0.$$

If we are correct in choosing the $^1P_1{}^\circ$ as the term perturbing the $^3P_1{}^\circ$ series, it must be assigned to the structure d^9s^2p. In that case, the corresponding $^3P_1{}^\circ$ must be considerably higher. This is the reverse of what would be expected from analogy with similar structures, e.g., d^9sp, d^9p. The $^1P_1{}^\circ$ series is interesting because its perturbation also explains the anomalous opening out of the isotope displacements observed by Schüler and Keyston.[7] The plot of n^*-n (Fig. 6) makes it evident that the term 5368 is the logical one to remove. The formula gives a very good agreement except for the low first member and the first one above the perturbation.

$$\nu_0 = 5368$$
$$\mu = -4.0425$$
$$\alpha = -1.587 \times 10^{-6}$$
$$\beta = -145.5$$
$$\text{Res.} = \sim -141, 0, 0, (\nu_0), -33, -5, 0, +1, -1, -2.$$

The observations of isotopic displacements indicate that they are greatest for terms arising from complicated structures. In Hg I, Schüler and Keyston observe an isotopic shift in the ^1S series, decreasing for higher members.

In the $^1P^\circ$ series they observe zero displacement for the lowest level, a large displacement for the level 5318 and a smaller one for 4217. Unfortunately their observations cannot include the second and third levels, 12886.2 and 7318. The second of these is given in the paper by Paschen quoted above. The level 5318 which shows the large displacement is the one now assigned to the complicated structure d^9s^2p. Its effect as a perturbing term must naturally be treated separately for each isotope, with the result that the series members will show isotopic displacements depending on their nearness to the perturbing term. The case is analogous to the opening out of the intervals in the ^3D series of Ca I. The presence of two $6s$ electrons seems to be requisite for a large isotopic displacement.

Al II

The spark spectrum of aluminium has been beautifully analysed by Sawyer and Paschen.[8] It is a two electron spectrum like calcium, and long series

[7] Schüler and Keyston, Zeits. f. Physik **72**, 423 (1931).
[8] Sawyer and Paschen, Ann. d. Physik **84**, 1 (1927).

of type $3snx$ have been recognised. In addition a number of terms have been found which originate in other structures. In particular, the $3p^2\ ^3P$ has been found and a $^3P^\circ$ combining with it. The latter term is incorrectly attributed to $3p3d$. Its position and intervals both indicate the origin $3p4s$.

In Fig. 7 are given the usual plots of all the series of Al II. By using a different scale for each series, the series have all been reduced to an arbitrary length of 100 to make their peculiarities more easily comparable. It is obvious that the ^3G series is accurately Ritzian, and that $^3S\,^1S\,^3D\,^1F^\circ$ and possibly $^3P^\circ$ are nearly so. The series $^3F^\circ\,^1D\,^1P^\circ$ are very far from being Ritzian, and all exhibit the rapid fall in n^*-n towards small term values, which is characteristic of perturbed series into which the perturbing term has been absorbed.

Let us consider the possible foreign terms. They are $3p4s\,^3P^\circ\,^1P^\circ$; $3p^2\ ^1S$, ^1D; $3p3d\,^3P^\circ$, $^3F^\circ$, $^1P^\circ$, $^1F^\circ$. Of these, the only one certainly known is $3P4s\,^3P^\circ$,

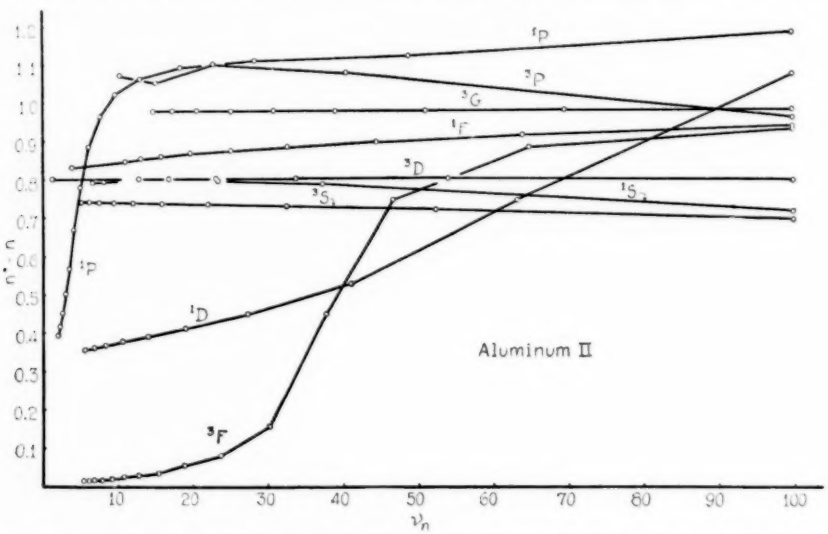

Fig. 7. Series of Al II. The horizontal scale is different for each series in order to reduce them to equal lengths for purposes of comparison. The ordinates of the ^1D series have been reduced by 0.5.

but the positions of the others can be reasonably estimated. From the known $p^2\ ^3P$, and by analogy with other spectra, we can place $s^2\ ^1D$ at about 50,000 to 56,000. The ^1D series contains terms at 66,381 and 41,773, one of which should be $p^2\ ^1D$. In this connection it should be remembered that the perturbing term is also itself displaced. For that reason we believe that the level 66381 is $p^2\ ^1D$, its position being so low because of the repulsion of all of the series terms. The displacement corresponds to a change of about 0.1 in the Rydberg denominator with respect to its own limit. The $p^2\ ^1S$ is either ineffective in producing a perturbation or it lies above the series limit.

The $^3P_2^\circ$ series is given as certain to the fifth member only, and is rather irregular even there. It is probably perturbed by the known $3p4s\,^3P_2^\circ$ at 5903 and also by $3d3p\,^3P^\circ$, the position of which will be discussed below. The $^1P^\circ$ has a disturbance between 5000 and 3000 and probably also above 2000. The

perturbations can be assigned to $3p4s\,^1P^\circ$ and $3d3p\,^1P^\circ$ both unidentified. The remaining irregular series is $^3F^\circ$. The perturbing term is almost certainly the one at 10700. Its separations are large and its position is correct for the term $3d3p^3F^\circ$. In that case $3d3p^3P^\circ$ should not be far away. At λ1910 in Sawyer and Paschen's list we find three lines with approximately the separations of $p^2\,^3P$. If we assume that they are the transition $p^2\,^3P - pd^3P^\circ$, and that the multiplet has the theoretical intensities, we obtain the approximate values

$$3p3d^3P_2^0\ 5262.8$$
$$^3P_0^1\ 5267.7$$
$$^3P_0^0\ 5266.8$$

The combination $4^3S - pd^3P^\circ$ would then fall about $\nu = 55326$ and there is an unidentified broad line at $\nu = 55328$. (λ1807.40). No other combinations are found, but we believe that the evidence is conclusive for the reality of that term. The $3snf\,^1F^\circ$ series shows a falling off of $n^* - n$ towards the end of the series which may indicate the presence of $3p3d\,^1F^\circ$ near the limit. As was remarked above, the $^1P^\circ$ series indicates a second perturbation above 2000 which is an indication that $3p3d\,^1P$ is also near the series limit. The remaining unidentified terms of this structure, $3p3d^3D^\circ$ and $^1D^\circ$, cannot perturb the ordinary D-series since the parities are opposite.

The calculations for the various perturbed series of Al II are as follows:

^1D Series

$$\nu_0 = 66381 = p^2\,^1D?$$
$$\mu = -0.3603$$
$$\alpha = 2.096 \times 10^{-6}$$
$$\beta = -1300$$
$$n = 3, 4 \text{ etc.}$$

$$\text{Residuals } \left(\frac{\nu_n}{4}\right)$$

$$(\nu_0),\ +55,\ 0,\ 0,\ -1,\ 0,\ 0,\ 0,\ 0,\ 0.$$

The only large deviation is at the usual point, i.e., in the term nearest to the perturbation.

$^1P_1^\circ$.

As was remarked above, this series is perturbed by $3p4s\,^1P^\circ$ and probably, above the known terms, by $3p3d\,^1P$. But the series has so completely absorbed the $3p4s\,^1P^\circ$ term that it is impossible, and indeed meaningless, to remove any one level from the series and assign it to that structure. The added complication of the probable higher unknown perturbing level makes a series calculation useless. As could be foreseen in such a case, no reasonable fit can be obtained, even though the assignment of any one of a number of terms as $3p4s\,^1P$ gives a curve resembling closely the usual hyperbola.

^3F.

In this series also, the perturbing term is rather intimately absorbed into the series, but it is possible to obtain a formula which gives a very reasonable agreement. The details are as follows. (Table V).

TABLE V. *Constants of* $^3F^\circ$ *series of Al II.*

Al II

$^3F_4^\circ$

$\nu_0 = 10720 = 3d3p^3F_4^\circ$
$\mu = -0.0579$
$\alpha = +0.575 \times 10^{-6}$
$\beta = -530$
$\eta = 4, 5, 6$
Res.$(\nu_n/4) = 0, +4, 0, (\nu_0), +20, +1, -1, +1, -3, 0, 0, +4, +2, +1, 0$

$^3F_3^\circ$

$\nu_0 = 10753$
$\mu = -0.0636$
$\alpha = 0.754 \times 10^{-6}$
$\beta = -536$
$\eta = 4, 5, 6$
Res.$(\nu_n/4) = 0, 0, 0, (\nu_0), +21, +1, -1, -1, -2.$

$^3F_2^\circ$

$\nu_0 = 10778$
$\mu = -0.0613$
$\alpha = 0.701 \times 10^{-6}$
$\beta = -550$
$\eta = 4, 5, 6$
Res.$(\nu_n/4) = 0, 0, 0, (\nu_0), +25, +4, 0, -1, 0.$

Cu I

The arc spectrum of copper contains probably the most distorted series known, the np^2P° series. The lowest member of that series produces the resonance lines in combination with $4s^2S$, and a single second member at 12933 with $J = 1\frac{1}{2}$ has also been recognised for a long time. The higher members of the series were only definitely settled when the spectrum had been so thoroughly analysed, that everything was accounted for except this series.[9] The evidence is now conclusive that the level at 12933 is, in reality, double and inverted, with a separation of about 0.4 wave numbers. The proof came from the accurate measurement of the $m^2D - 5^2P^\circ$ combination lines by Burns[10] and the observation that the Zeeman effect of λ2024 $1^2S - 5^2P^\circ$ is a Paschen-Back effect. The character of the higher members is fixed by Selwyn's[11] observation of the $1^2S - n^2P^\circ$ combinations in the Schumann region; and, in some cases, by Zeeman effects observed by one of us (A.G.S.) Fig. 8 is the plot of the $n^* - n$ against ν_n. The $J = 1\frac{1}{2}$ component is evidently strongly perturbed between the third and fourth members and the $J = \frac{1}{2}$ between the fourth and fifth. In just those positions 5973 and 3952 there are the two components of a wide $^2P^\circ$ arising from $3d^94s4p$. The higher series

[9] Shenstone, Phys. Rev. **34,** 1623 (1929).
[10] Burns, Allegheny Obs. Publications VIII 3.
[11] Selwyn, Proc. Phys. Soc. London **41,** 392 (1929).

members are not known with sufficient accuracy or in sufficient number to warrant an accurate calculation of Langer's formula, but a rough calculation gives an approximate fit with the constants for the two series about -100 and -200. There should be also a perturbation due to another $^2P^\circ$ from the same structure, but its effect is evidently much smaller. One would also expect a large perturbation in the nf^2F° series. There are only two members of that

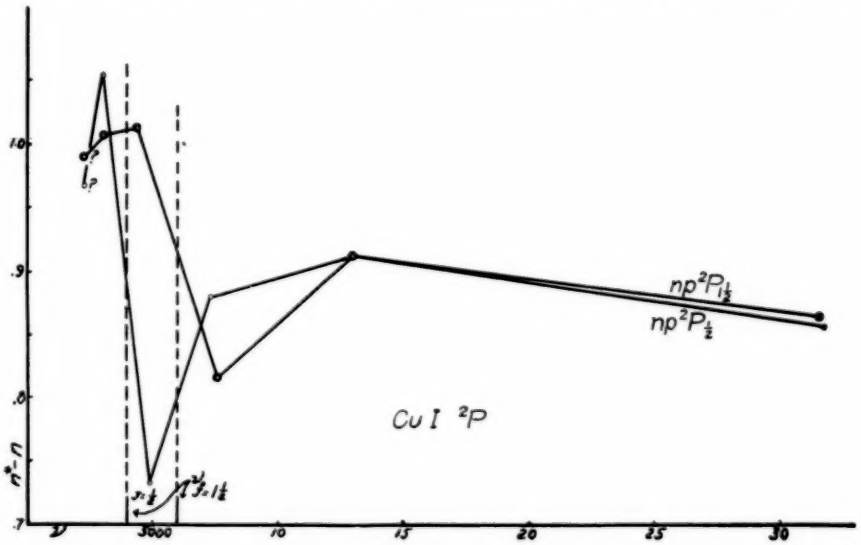

Fig. 8. $^2P^0$ series of Cu I.

series certainly known but they are just in the position to make the perturbation evident, if it existed. The lower of the two levels does show a small inversion but otherwise both members are practically Rydbergian. The exact reverse of this phenomenon is shown in the spectra Zn II and Cd II[12] which are equivalent in structure to Cu I. The $^2P^\circ$ series are quite regular, but the $^2F^\circ$ series exhibit perturbations. From the positions of the irregularities it can be predicted with reasonable certainty that there should be found the following terms in those two spectra.

Zn II

$3d^9 4s 4p\ ^2F^0_{3\frac{1}{2}} \sim 13500$

$^2F^0_{2\frac{1}{2}} \sim 10500$

Cd II

$4d^9 5s 5p\ ^2F^0_{3\frac{1}{2}} \sim 8500$

$^2F^0_{2\frac{1}{2}} \sim 3000$

There are without doubt many other known series where the methods used in this paper will reveal the presence of perturbations. For instance, the ^2D of Al I certainly contains an extra term whose origin can be safely ascribed to the structure $3s3p^2$. The Mg I ^1D series includes $p^2\ ^1D$ at 2631.6.[13]

[12] Takahashi, Ann. d. Physik **3**, 27 (1929).

[13] Sawyer, J.O.S.A. **13**, 431 (1926).

The Sr I $^1P^\circ$ series is exactly analogous to Ca I $^1P^\circ$. The second member, 11838.7, gives an anomalously weak line in combination with ^1S, but the curve for the series indicates that the level at 3474.7 is causing the perturbation. The ^1S of Sr I is perturbed by $p^2\ ^1S$ at 8765.2. The ^3D of Sr I indicates the presence beyond the known terms of $4d6s^3D$, which can, from energy considerations, be placed in the neighborhood of 800.

While this paper was in preparation there appeared an analysis of the spectrum C III by Edlen.[14] The series contain several good examples of the type of disturbance described in this paper. It will be noticed that $2p3p^3S$ perturbs the ordinary ^3S series; $2p3p^3D$ perturbs the ^3D series and produces the very wide separations in the second member; $2p3d^3F^\circ$ perturbs the $^3F^\circ$ series. Other disturbances might be expected but are not found, e.g., the $^3P^\circ$ series by $2p3s^3P^\circ$.

It is probable that, in the spectra Ga II[15] and In II[16], which are similar to Al II, the $p^2\ ^1D$ is the level assigned as the first member of the ordinary ^1D series.

The spectrum of lead[17] is interesting because the perturbations are between terms of similar electron structure. In it we have series of terms based on the $^2P_{\frac{1}{2}}$ limit perturbed by terms based on the $^2P_{1\frac{1}{2}}$ limit. Very few of the latter terms have been found and the presence of the perturbations may easily lead to new identifications. A similar type of perturbation is probably the cause of irregularities in Ne I, A I, etc.

In the following table (Table VI) there are collected the constants for all the series which have been considered in any detail. In comparing the values of the constants α and β, it should be noticed that in Al II, the values of α must be multiplied by 4 and β divided by 4 to make them comparable with arc spectrum values.

A review of the data of Table VI discloses the fact that the constant β is always negative. This is the same as saying that the foreign level attempts, by repulsion of neighboring terms, to make a place for itself in the series. The effect is strikingly shown in Fig. 3. In value, β ranges from -3 to -1200 but in most cases is in the range from -25 to -150 wave numbers.

The theoretical problem presented by the failure of perturbations to occur is perhaps more important than the fact that many do occur. Some cases have been noted in the discussion of particular spectra but many more can certainly be found. The problem is being investigated in this laboratory from both the theoretical and the experimental sides.

It is evident from the data given that there are two places in a perturbed series which show poor agreement with the simple formula. The first disagreement is in the lowest term of the series. This is quite common in unperturbed series and will be discussed below. The second disagreement is in the terms next to the perturbing term. It might be assumed that this deviation could

[14] Edlen, Zeits. f. Physik **72**, 559 (1931).
[15] Sawyer and Lang, Phys. Rev. **34**, 712 (1929).
[16] Lang and Sawyer, Zeits. f. Physik **71**, 453 (1931).
[17] Giessler and Grotrian, Zeits. f. Physik **39**, 377 (1926).

TABLE VI. *Adopted series formula.* $n^* = n + \mu + \alpha\nu_n + (\beta/\nu_n - \nu_0)$. Constants for all the series which have been considered in detail. In the case of Al II, α should be multiplied by 4 and β divided by 4 to make them comparable with arc spectrum constants.

Spectrum	Series	μ	α	β	ν_0	(origin)	Remarks
Ca I	^1S	−2.3495	-1.066×10^{-6}	−100	8614	p^2	
	$^1P^\circ$ (a)	∽−2.291	∽2.7×10^{-5}	∽−4500	12573	$3d4p$	Questionable
	(b)	−1.9753	1.42×10^{-7}	−526	5372	?	Questionable
	$^3P_2^\circ$	−1.9489	-7.48×10^{-6}	−62.9	9964	$3d4p$	
	^1D	∽−0.8678	∽-4.4×10^{-6}	∽−150	8585	$4p^2$	Probably a second pert. at 1492 (d^2)?
	$^3D_3$	−0.8656	-3.665×10^{-6}	−90	1829	$3d5s$	
	$^3D_2$	−0.8678	-3.571×10^{-6}	−86	1839	$3d5s$	
	$^3D_1$	−0.8705	-3.39×10^{-6}	−85	1849	$3d5s$	
	$^1F^\circ$	−0.0955	2.90×10^{-5}	−80	8767	$3d4p$	
Ba I	$^3F_4^\circ$	−0.1980	8.33×10^{-6}	−33	4900.5	$5d7p$	
	$^3F_3^\circ$	−0.1956	8.016×10^{-6}	−32.3	5521.2	$5d7p$	
	$^3F_2^\circ$	−0.1934	7.23×10^{-6}	−28	5797.3	$5d7p$	
	$^1F_3^\circ$	−0.1497	5.25×10^{-6}	−31.5	4292.4	$5d7p$	
	$^1P^\circ$	−3.9192	4.635×10^{-6}	−1179	13478	$3d6p$	
				−150	3532	$3d7p$	Two perturbations
Hg I	$^3P_2^\circ$ (a)	−4.0093	-1.152×10^{-5}	−365	15295	$5d^{9}6s^26p$	Reversal of roles of these two levels
	(b)	−4.0842	-1.129×10^{-5}	−150	12974	$5d^{9}6s^26p$	
	$^3P_1^\circ$ (a)	−4.1900	-4.15×10^{-6}	−3	7273?	$5d^{9}6s^26p^3P_1^\circ$	Questionable level
	(b)	−4.1925	-4.02×10^{-6}	−6	5368	$5d^{9}6s^26p^1P_1^\circ$	$J-J$ coupling.
	$^1P^\circ$	−4.0425	-1.587×10^{-6}	−145.5	5368	$5d^{9}6s^26p^1P_1^\circ$	
Al II	$^1P^\circ$	∽−0.85	∽-0.3×10^{-6}	∽−400	3858?	$3p4s$	Very approximate
	^1D	−1.3603	2.096×10^{-6}	−1300	66381	$3p^2$	
	$^3F_4^\circ$	−0.0579	$+0.575\times10^{-6}$	−530	10720	$3p3d$	
	$^3F_3^\circ$	−0.0636	$+0.754\times10^{-6}$	−536	10753	$3p3d$	
	$^3F_2^\circ$	−0.0613	$+0.701\times10^{-6}$	−550	10778	$3p3d$	
Cu I	$^2P_{\frac{3}{2}}^\circ$	∽−2.0572	∽-0.69×10^{-6}	∽−196	3952	$3d^{9}4s4p$	Approximate only
	$^2P_{1\frac{1}{2}}^\circ$	∽−2.0404	∽-2.56×10^{-6}	∽−100	5973	$3d^{9}4s4p$	Approximate only

be removed by the consideration of an expression of type $\gamma/(\nu_n-\nu_0)^2$. Such can not be the case, however, because the deviation is never symmetrical and the large error frequently occurs for the term which is the further from the perturbation. The plot of the parabola $(n^*-n)\ (\nu_n-\nu_0)$ against ν_n, usually tells unambiguously which level it will be impossible to fit on the curve. In other words, it is not merely a question of fitting the formula to one or the other term by a change in the constants. It is really impossible to fit any formula of Langer's type without modification to give agreement at the points which, in the calculated series, show the large deviations.

As regards the large deviations from the Ritz formula shown by the first members of both regular and irregular series, it should be remarked that there is a very great distinction between one and two electron spectra. If one plots the curves for Na, K, Rb, Cs, ^2S, and $^2P^\circ$ series, the lack of linearity is very small indeed. The reverse is the case for the ^1S and $^3P^\circ$ series of Mg, Zn, Cd, Hg. The lowest terms are normally thousands of wave numbers below the position indicated by a linear extrapolation. The comparison is roughly as follows:

$^2P^0$ Na, K, Rb, Cs $= 0, 0 \sim 40 \sim 90$
^2S " " " " $= 0\ 0\ 0\ 0$
$^3P^0$ Mg Zn Cd Hg ~ 0 2300, 2200, 3500
^1S " " " " $\sim$ 6800, 9300, 8700, 9500.

The series of Ca, Sr. Ba are too perturbed to be of value in this comparison. It is also perhaps unfair to use the ^1S series at all, because the lowest member is due to a closed group s^2. The P series however show very clearly that the tendency of series is quite different in the one and two electron spectra.

Langer remarks that his result

$$n^* = n + \sum \frac{p_{in}}{\nu_n - \nu_i}$$

is obtained from a consideration of the perturbation theory for more than one electron. If we accept the experimental result from perturbed series that the p_{in} are always of such a sign as to cause repulsion, the lowest term of a series in a two-electron system experiences repulsions from all the higher members with no compensating repulsions from lower terms. One would then expect to find it moved toward lower term values, i.e., smaller values of n^*. This is in agreement with observation.

The numerical computations in this paper were greatly facilitated by a Rydberg term table calculated by Miss Janet MacInnes in this laboratory. The table contains the values of R_∞/n^{*2} for values of n^* from 1 to 11 in steps of 0.001. Fowler's table in steps of 0.01 and Paschen's table in steps of 0.05 are not sufficiently detailed to allow a linear interpolation. In one series, which was first calculated by using Fowler's table, errors of as much as 8 wave-numbers were detected when it was recalculated on the basis of the new table.

Miss MacInnes and Professors Condon and Turner have been very helpful in the preparation and criticism of this paper.

WAVE MECHANICS OF RADIATION AND FREE PARTICLES

By E. H. Kennard
Department of Physics, Cornell University

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Abstract

The quantum theory of radiation, formulated in wave-mechanical language but in terms of running waves, is shown to lead under suitable conditions to the classical theory of emission by a particle as a first approximation. Non-relativistic mechanics is used, and the limitations of the method are brought out in terms of classical theory. The characteristic quantum phenomenon of the Compton effect requires that the Compton recoil shall exceed the spread in momentum of the particle, and so that the wave-packet shall greatly exceed in diameter the wave-length of the incident radiation; this condition is realizable on any scale of magnitude. For quasi-classical motion just the reverse is required; furthermore, if the motion is to last for a number of wave-periods, the wave-length must greatly exceed h/mc (m = mass of the particle). The classical packet-motion arises from combinations between quantum-states of the particle-field system; this fact suggests that the photon is not a fundamental constituent of the field but only one possible aspect of its action. The infinite "zero-energy" associated apparently even with the lowest energy-state of the field implies no electromagnetic field intensities at any point. Whereas for problems on energy or momentum it is customary to represent an incident wave-train by a single typical quantum state, to obtain motional phenomena of classical type a more complete expression such as that given in the paper must be used. The physically empty field likewise corresponds to a mixture of quantum states but without correlation among their amplitudes.

THE quantum-mechanical theory of radiation initiated by Dirac, which yields a correct formula for the quantum phenomenon of the Compton effect, must likewise lead to the classical theory of radiation as an approximation valid under certain conditions. A certain theoretical interest seems to attach to the manner in which it does this. In particular, one would like to see how we can bring under the same theoretical roof the continuous oscillation, chiefly along the electric vector, of a free electron in a Hertzian wave-train, on the one hand, and the billiard-ball Compton recoil of an electron on the other, both occurring in radiation fields that appear to differ only in respect of wave-length.[1] Such a discussion forms the object of the present paper. A wave-mechanical form of the theory, new in some details, is employed, partly because wave-mechanics seems less repellently abstract to many than the more usual symbolic matrix formulation; and the treatment is non-relativistic throughout. The mathematical machinery remains, nevertheless, in spite of every simplification rather voluminous,[2] and is given only in skeleton; it is hoped that those who are interested chiefly in the ideas involved will find no difficulty in following the discussion while those who wish to follow the

[1] Cf. A. H. Compton, Phys. Rev. **31,** 59 (1928).
[2] Cf. W. Heisenberg, Ann. d. Physik **9,** 338 (1931).

mathematics in detail will have no trouble in following directions and filling in the gaps.

The classical theory of the field in Hamiltonian form is first developed as a prototype in greater detail than has been done elsewhere; then wave-mechanical formulas are deduced for the motion of the packet centroid in a radiation field, and from these the classical emission-formula for a point charge is obtained as an approximation. Letting this charge recede to infinity we have a typical quantum-mechanical expression for a physical plane wave-train. The paper closes with a brief discussion of the relation between the Compton effect and the classical law of force.

Classical Theory in Hamiltonian Form

A pure radiation field, characterized as such by the absence of electric charges in it, can be described completely in terms of a vector potential $\boldsymbol{A}$; and it can further be resolved into an infinite set of plane wave-trains running in all directions, that is, we can write:

$$\boldsymbol{A} = \int [\boldsymbol{a}'(\nu, \boldsymbol{n}) \cos 2\pi\nu(t - \gamma \boldsymbol{n}\cdot\boldsymbol{x}) + \boldsymbol{a}''(\nu, \boldsymbol{n}) \sin 2\pi\nu(t - \gamma \boldsymbol{n}\cdot\boldsymbol{x})]d\omega, \quad (1)$$

in which ν = frequency, $c = 1/\gamma$ = speed of light, $\mathbf{x}$ is the vector distance of the field-point from the origin, $\boldsymbol{n}$ is a unit vector in the direction of the element of solid angle $d\omega$ and $\boldsymbol{a}'$ and $\boldsymbol{a}''$ are vector functions of ν and $\boldsymbol{n}$ perpendicular to each other and to $\boldsymbol{n}$; the integral extends over all positive ν and all directions of $\boldsymbol{n}$. Associated with each pair of values of ν and $\boldsymbol{n}$ there are thus two wave-trains polarized at right angles. For the energy in the field one finds by means of Maxwell's equations, the formulas $\boldsymbol{E} = -\gamma\partial\boldsymbol{A}/\partial t$, $\boldsymbol{H}$ = curl $\boldsymbol{A}$, and a simple application of the divergence theorem:

$$W_0 = \int (E^2 + H^2)/8\pi d\tau = (\gamma^2/8\pi) \int [(\partial\boldsymbol{A}/\partial t)^2 - \boldsymbol{A}\cdot\partial^2\boldsymbol{A}/\partial t^2]d\tau,$$

the field being assumed to vanish fast enough at infinity so that $\int \text{div } \boldsymbol{A}\times\boldsymbol{H}d\tau = 0$. We now substitute here for $\boldsymbol{A}$ from (1), replace ν and ω as variables in one integral by $\nu n_x, \nu n_y, \nu n_z$ (so that $\nu^2 = (\nu n_x)^2 + (\nu n_y)^2 + (\nu n_z)^2$ and $\nu^2 d\nu d\omega$ = element of volume in polars $= d(\nu n_x)d(\nu n_y)d(\nu n_z)$), and evaluate the result by means of repeated applications of the Fourier integrals,

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} f(\mu') \cos 2\pi x(\mu' - \mu)d\mu' = f(\mu),$$

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} f(\mu') \sin 2\pi x(\mu' - \mu)d\mu' = 0. \quad 2)$$

The final result is an expression for the energy of the field in terms of the amplitudes a' and a'' of the wave-trains, viz.,

$$W_0 = (\pi c/2) \int (a'^2 + a''^2)d\nu d\omega. \quad (3)$$

In order to apply quantum theory we must now substitute for Maxwell's equations a statement of the laws of the field in Hamiltonian form, that is, we must describe the field in terms of variables obeying the Hamiltonian equations of motion. For simplicity we shall make these finite in number by replacing our continuous set of wave-trains by a discrete set, associated in pairs with equal intervals $\Delta\nu$ on the frequency axis and equal elements of solid angle $\Delta\omega$ in direction; the integrals above are then to be replaced by sums. Then at the end of our calculations we let $\Delta\nu$ and $\Delta\omega$ approach zero. There is a considerable range of choice for the Hamiltonian variables, but all must lead to the same result. The simplest choice for wave-mechanical purposes[3] seems to be to take as variables describing the wave-trains associated with given ν and $\boldsymbol{n}$ the two pairs:

$$\begin{aligned} Q' &= Ba' \cos 2\pi\nu t \qquad Q'' = Ba'' \sin 2\pi\nu t \\ P' &= -Ba' \sin 2\pi\nu t \qquad P'' = Ba'' \cos 2\pi\nu t \end{aligned} \tag{4}$$

where $B=(c\Delta\nu\Delta\omega/2\nu)^{1/2}$. It will be more convenient, however, to number these pairs of variables in a single sequence, merely remembering that two members of the sequence belong to each ν and $\boldsymbol{n}$. Eqs. (1) and (3) then become, in terms of these coordinates:

$$\boldsymbol{A} = \sum(\sigma)\boldsymbol{b}_\sigma(Q_\sigma \cos \gamma\mu_\sigma x_\sigma - P_\sigma \sin \gamma\mu_\sigma x_\sigma), \tag{5}$$

$$W_0 = \sum(\sigma)\pi\nu_\sigma(Q_\sigma^2 + P_\sigma^2), \tag{6}$$

where $\mu_\sigma = 2\pi\nu_\sigma$, $\boldsymbol{n}_\sigma$ is the unit ray-vector for wave-train number σ, $x_\sigma = \boldsymbol{n}_\sigma \cdot \boldsymbol{x}$, $\boldsymbol{b}_\sigma = (2\nu_\sigma\Delta\nu\Delta\omega/c)^{1/2}\boldsymbol{l}_\sigma$, $\boldsymbol{l}_\sigma$ being a unit vector in the direction of the electric vector (i.e., of the original $\boldsymbol{a}'$ or $\boldsymbol{a}''$). Obviously with W_0 as Hamiltonian the new variables obey the Hamiltonian equations: $\dot{Q}_\sigma = \partial W_0/\partial P_\sigma$, $\dot{P}_\sigma = -\partial W_0/\partial Q_\sigma$.

For the treatment of physical problems it is necessary to introduce electricity into the field, contrary to our assumption that there is none there. It was tacitly assumed by Dirac[4] that this inconsistency would not invalidate the results so far as concerns pure radiation effects; we shall see presently to what extent this assumption is justified. Accordingly we add the usual (non-relativistic) expression for one or more independent particles having charges e_j and masses m_j and obtain as the classical Hamiltonian function for a number of particles interacting only by way of the radiation field:

$$W = \sum(\sigma)\pi\nu_\sigma(Q_\sigma^2 + P_\sigma^2) + \sum(j)(1/2m_j)(\boldsymbol{p}_j - \gamma e_j \boldsymbol{A}_j)^2, \tag{7}$$

where $\boldsymbol{A}_j$ stands for $\boldsymbol{A}$ with the coordinates of particle no. j inserted for $\boldsymbol{x}$, $\boldsymbol{p}_j$ is the vector generalized momentum for the jth particle, and $\Sigma(j)$ extends over all particles.

It is well known that the second term in W as given by (7) yields correct values for the motion of the particles themselves in a given field with vector

[3] Similar variables are employed by Born and Jordan in their book, Quantenmechanik, but they employ standing waves inside a box in place of running waves.

[4] P. A. M. Dirac, Roy. Soc. Proc. **114**, 243 (1927).

potential $\boldsymbol{A}_j$, the velocity of the jth particle being $\boldsymbol{v}_j=(\boldsymbol{p}_j-\gamma e_j\boldsymbol{A}_j)/m_j$. We shall treat here the converse case, the reaction of the particle upon the field according to classical theory, doing this partly because the calculations will serve as a valuable guide in the quantum work and partly to reveal the nature of the limitations upon Dirac's hypothesis. For simplicity we shall assume but one particle present; the extension to many is easy. We have then:

$$\begin{aligned}\dot{Q}_\sigma &= \frac{\partial W}{\partial P_\sigma} = 2\pi\nu_\sigma P_\sigma + \frac{e}{cm}\left(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\right)\cdot\boldsymbol{b}_\sigma \sin\gamma\mu_\sigma x_\sigma,\\ \dot{P}_\sigma &= -\frac{\partial W}{\partial Q_\sigma} = -2\pi\nu_\sigma Q_\sigma + \frac{e}{cm}\left(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\right)\cdot\boldsymbol{b}_\sigma \cos\gamma\mu_\sigma x_\sigma.\end{aligned} \tag{8}$$

Let us suppose that the field vanishes until $t=0$, when the charge begins to move. The appropriate solution of (8) is,

$$Q_\sigma + iP_\sigma = \gamma e\int_0^t \boldsymbol{b}_\sigma\cdot\boldsymbol{v}\,[\sin\mu_\sigma(t-t'+\gamma x_{\sigma e}) + i\cos\mu_\sigma(t-t'+\gamma x_{\sigma e})]dt', \tag{8a}$$

where $\boldsymbol{v}=(\boldsymbol{p}-e\boldsymbol{A}/c)/m$, and by (5) the resulting potential is:

$$\boldsymbol{A} = 2e\gamma^2\sum(\sigma)\nu_\sigma\Delta\nu\Delta\omega\boldsymbol{I}_\sigma\int_0^t \boldsymbol{I}_\sigma\cdot\boldsymbol{v}\sin\mu_\sigma(t-t'+\gamma x_{\sigma e}-\gamma x_\sigma)dt', \tag{9}$$

in which $\boldsymbol{v}$ and $x_{\sigma e}$ stand for values at the particle and at time t' while x_σ refers to the field-point at which $\boldsymbol{A}$ is given by the equation. Now if $\boldsymbol{B}$ is any vector and if we denote the two perpendicular $\boldsymbol{I}$'s that belong to given ν_σ and $\boldsymbol{n}_\sigma$ by $\boldsymbol{I}_{\sigma 1}$, $\boldsymbol{I}_{\sigma 2}$, we have

$$\boldsymbol{I}_{\sigma 1}\cdot\boldsymbol{B}\,\boldsymbol{I}_{\sigma 1} + \boldsymbol{I}_{\sigma 2}\cdot\boldsymbol{B}\,\boldsymbol{I}_{\sigma 2} = \boldsymbol{B}_{\perp\sigma} \tag{10}$$

where $\boldsymbol{B}_{\perp\sigma}$ denotes the vector component of $\boldsymbol{B}$ perpendicular to $\boldsymbol{n}_\sigma$. Hence

$$\boldsymbol{A} = 2e\gamma^2\int_0^\infty \nu_\sigma d\nu_\sigma\int d\omega\int_0^t \boldsymbol{v}_{\perp\sigma}\sin\mu_\sigma(t-t'+\gamma x_{\sigma e}-\gamma x_\sigma)dt'.$$

The integration over $d\omega$ is easily carried out first. We note that $\int\boldsymbol{v}_{\perp\sigma}\sin\mu_\sigma\gamma(x_{\sigma e}-x_\sigma)d\omega$ vanishes by symmetry, $\boldsymbol{v}_{\perp\sigma}$ being the same and $x_{\sigma e}-x_\sigma$ reversed in sign for trains moving oppositely. Hence

$$\boldsymbol{A} = 2e\gamma^2\int_0^\infty \nu_\sigma d\nu_\sigma\int_0^t dt'\int\boldsymbol{v}_{\perp\sigma}\sin\mu_\sigma(t-t')\cos\mu_\sigma\gamma(x_{\sigma e}-x_\sigma)d\omega.$$

Now let $\boldsymbol{r}$ denote distance from the particle to the field-point and take this line as the axis of polars. Then $\cos\mu_\sigma\gamma(x_{\sigma e}-x_\sigma)=\cos(\mu_\sigma\gamma r\cos\theta)$, θ referring to the direction of $\boldsymbol{n}_\sigma$, $\boldsymbol{v}_{\perp\sigma}=\boldsymbol{v}-\boldsymbol{v}\cdot\boldsymbol{n}_\sigma\boldsymbol{n}_\sigma=\boldsymbol{v}-(v_r\cos\theta-v_\perp\sin\theta\cos\phi)\boldsymbol{n}_\sigma$, $\boldsymbol{v}_r$ and $\boldsymbol{v}_\perp$ being vector components respectively parallel and perpendicular to $\boldsymbol{r}$, $d\omega=\sin\theta d\theta d\phi$; and after several partial integrations over θ, and then one in the $1/r^3$ terms with respect to ν_σ, one finds that several terms cancel and

$$\boldsymbol{A} = 2e\gamma^2 \int_0^\infty dv_\sigma \int_0^t \left[\frac{2\boldsymbol{v}_\perp}{\gamma r} \sin \mu_\sigma (t - t') + \frac{2v_r - v_\perp}{\pi \nu_\sigma \gamma^3 r^3} (t - t') \cos \mu_\sigma (t - t') \right] \sin \mu_\sigma \gamma r dt'$$

in which v_r, $\boldsymbol{v}_\perp$ and r are all functions of t'. We next replace the product of sines or cosines by functions of $t - t' \pm \gamma r$, change the variable of integration by means of the formula, $d(t' \mp \gamma r) = (1 \pm \gamma v_r) dt'$, and then apply the formulas:

$$\int_0^\infty d\mu_\sigma \int_0^T f(\tau) \cos \mu_\sigma (\tau - k) d\tau = \lim_{\mu \to \infty} \int_0^T f(\tau) \frac{\sin \mu(\tau - k)}{\tau - k} d\tau = \pi f(k) \text{ or } 0$$

according as $0 < k < T$ or not, k and T being constants; and

$$\int_0^\infty \frac{dv_\sigma}{v_\sigma} \sin M v_\sigma = \frac{\pi}{2} \text{ if } M > 0 \text{ and } = -\frac{\pi}{2} \text{ if } M < 0.$$

We thus find that for $t > \gamma r$

$$\boldsymbol{A} = \frac{e}{c} \left(\frac{\boldsymbol{v}_\perp}{r(1 - \gamma v_r)} \right)_{t - \gamma r} + ec \int_{t - \gamma r}^t \frac{2v_r - \boldsymbol{v}_\perp}{r^3} (t - t') dt', \qquad (11)$$

while for $0 < t < \gamma r$

$$\boldsymbol{A} = ec \int_0^t \frac{2v_r - \boldsymbol{v}_\perp}{r^3} (t - t') dt'.$$

$\boldsymbol{A}$ as given by (11) should represent at least the radiative component of the field around a point-charge moving with variable velocity $\boldsymbol{v}$. It is immediately obvious, that the result cannot be entirely correct, for the second term is not properly retarded. Even the first term has an unfamiliar look; but this is merely a consequence of the fact that our wave-trains must necessarily yield a solenoidal potential whereas in the usual theory div $\boldsymbol{A}$ does not always vanish; upon differentiating the first term one nevertheless obtains correct values for the electric and magnetic fields in so far as they are of order $1/r$. The true magnitude of the error is best appreciated by passing to the case of simple harmonic motion. If we put $\boldsymbol{v} = \boldsymbol{v}_0 \sin 2\pi\nu_0 t$, where $\boldsymbol{v}_0$ is small, the integral in (11) is easily evaluated (r being treated as sensibly constant). Omitting details we shall merely state here that the result represents the correct Hertzian electric and magnetic fields around a vibrating doublet of instantaneous moment $-e\boldsymbol{v}_0 \cos 2\pi\nu_0 t / 2\pi\nu_0$, starting from rest at $t = 0$, *except* that there is superposed upon this field for $t > 0$ the static electric field of a doublet of instantaneously equal and opposite moment, and also out to $r = ct$ the same for a doublet of moment $-e\boldsymbol{v}_0 / 2\pi\nu_0$. The error is thus of order $(r/\lambda_0)^3$, $\lambda_0 = c/\nu_0$. (The complete classical field would likewise contain, of course, the simple electrostatic field of the particle.)

In general, then, in classical theory the application of the Hamiltonian

equations to the running-wave formulation gives correctly the radiation field around a moving point-charge at distances rather large relative to all the principal wave-lengths involved in the Fourier representation of the motion of the charge. This restriction excludes the simple case of a charge in uniform relative motion, and it also prevents, unfortunately, any application to the problem of radiation reaction.

Wave Mechanics of the Radiation Field

To apply wave mechanics we now introduce a wave-scalar ψ, which is a function of the Q's, the coordinates of the particles and the time, and form a Schrödinger equation for it in the usual way, assuming that W as given by (7) is the correct Hamiltonian so long as the particles interact only indirectly by way of the radiation field. The equation reads:

$$-\epsilon\frac{\partial\psi}{\partial t} = \sum(\sigma)\pi\nu_\sigma\left(\epsilon^2\frac{\partial^2}{\partial Q_\sigma{}^2}+Q_\sigma{}^2\right)\psi+\sum(j)\frac{1}{2m_j}\left(\epsilon\nabla_j-\frac{e_j}{c}\boldsymbol{A}_j\right)^2\psi, \quad (12)$$

where $\epsilon=h/2\pi i$, the subscript j on ∇ and $\boldsymbol{A}$ specifies that the space coordinates occurring therein are those of the jth particle, and $\boldsymbol{A}$ is the operator vector-potential:

$$\boldsymbol{A} = \sum(\sigma)\boldsymbol{b}_\sigma R_\sigma, \quad R_\sigma = Q_\sigma\cos\gamma\mu_\sigma x_\sigma-\epsilon\frac{\partial}{\partial Q_\sigma}\sin\gamma\mu_\sigma x_\sigma. \quad (13)$$

We shall presently deduce formulas for the motion of packets directly from this equation, but it seems impossible to make use of them without resorting to the usual cumbrous resolution into characteristic functions. The latter may be summarized as follows.

The Hamiltonian for the field alone, $W_0=\Sigma(\sigma)\pi\nu_\sigma(Q_\sigma{}^2+P_\sigma{}^2)$, is that for a collection of independent harmonic oscillators, expressed in what might be called "canonical form"; accordingly we have, as usual, as characteristic functions for the field alone

$$U_s(Q,N) = \eta(Q_1,N_{1s})\eta(Q_2,N_{2s})\cdots,$$

where $N_{\sigma s}$ denotes a particular choice of the N_σ's and $\eta(Q_\sigma,N_\sigma)$ stands for a normalized characteristic solution of the harmonic-oscillator equation:

$$\pi\nu_\sigma(Q_\sigma{}^2-h^2/4\pi^2\partial^2/\partial Q_\sigma{}^2)\eta(Q_\sigma,N_\sigma) = (N_\sigma+\tfrac{1}{2})h\nu_\sigma\eta(Q_\sigma,N_\sigma).$$

Inserting then M particles with vector coordinates $\mathbf{x}_j$ and momenta $\boldsymbol{p}_j$, we can write:

$$\psi = h^{-3M/2}\sum(s)U_s\int a(s\boldsymbol{p})e^{\zeta(\Sigma\boldsymbol{p}\cdot\mathbf{x}-W_{sp}t)}$$

$$= h^{-3M/2}\sum(s)U_s e^{-\zeta W_s t}\int\alpha(s\boldsymbol{p})e^{\zeta\Sigma\boldsymbol{p}\cdot\mathbf{x}}dp. \quad (14)$$

where $\zeta=1/\epsilon=2\pi i/h$, $W_s=\Sigma(\sigma)(N_{\sigma s}+1/2)h\nu_\sigma$, $W_{sp}=W_s+\Sigma(j)p_j{}^2/2m_j$, $\Sigma\boldsymbol{p}\cdot\mathbf{x}$ stands for $\Sigma(j)\boldsymbol{p}_j\cdot\mathbf{x}_j$, and the integration extends over all components of mo-

mentum of all particles; $\alpha(s\boldsymbol{p}) = a(s\boldsymbol{p}) \exp(-\zeta\Sigma(j)p_j^2 t/2m_j)$, both α and a being functions of s and the momenta of all particles and normalized so that

$$\Sigma(s)\int a^*(s\boldsymbol{p})a(s\boldsymbol{p})dp = \Sigma(s)\int \alpha^*(s\boldsymbol{p})\alpha(s\boldsymbol{p})dp = 1. \tag{15}$$

To find the time-variation of the coefficient α due to the interaction terms in (12) we substitute for ψ from (14) in (12) and select a particular coefficient in the usual way, by multiplying by a particular $U_s e^{-i\Sigma \boldsymbol{p}\cdot\boldsymbol{x}}$ and integrating over all Q's and x's; the orthogonality relations for the x's are expressed by the Fourier formulas (2). For the operator R we note that according to well-known recurrence relations

$$\begin{aligned} Q\eta(N) &= (h/4\pi)^{1/2}[N^{1/2}\eta(N-1) + (N+1)^{1/2}\eta(N+1)], \\ d\eta(N)/dQ &= (\pi/h)^{1/2}[N^{1/2}\eta(N-1) - (N+1)^{1/2}\eta(N+1)], \end{aligned}$$

with $\eta(-1) = 0$, whence

$$R_\sigma U_s = (h/4\pi)^{1/2}[N_\sigma{}^{1/2}U(s_\sigma^-)e^{i\mu_\sigma\gamma x_\sigma} + (N_\sigma+1)^{1/2}U(s_\sigma^+)e^{-i\mu_\sigma\gamma x_\sigma}, \tag{16}$$

where $U(s_\sigma{}^\pm)$ stands for U_s with $\eta(Q_\sigma, N_\sigma \pm 1)$ substituted in it for $\eta(Q_\sigma, N_\sigma)$; the extension of this formula to $R_\tau R_\sigma U_s$ is easy. The exponentials in x_σ introduce a "Compton shift," expressed by (18) below, in the $\boldsymbol{p}$ occurring in $\boldsymbol{b}_\sigma \cdot \boldsymbol{p}$, but this has no effect because $\boldsymbol{b}_\sigma \cdot \boldsymbol{n}_\sigma = 0$. We thus find eventually for the rate of change of α

$$\begin{aligned} (\dot{\alpha}sp) = &- \Sigma(j)\zeta p_j^2/2m_j \\ &+ \Sigma(j)\zeta e_j/cm_j(h/4\pi)^{1/2}\Sigma(\sigma)\boldsymbol{b}_\sigma\cdot\boldsymbol{p}[(N_{\sigma s}+1)^{1/2}\alpha(s_\sigma^+, \boldsymbol{p}_{j\sigma}^-)e^{-i\mu_\sigma t} \\ &+ N_{\sigma s}{}^{1/2}\alpha(s_\sigma^-\boldsymbol{p}_{j\sigma}^+)e^{i\mu_\sigma t}] - \Sigma(j)ie_j^2/4c^2m_j\Sigma(\sigma,\tau)\boldsymbol{b}_\sigma\cdot\boldsymbol{b}_\tau \\ &\quad [(N_{\sigma s}+1)^{1/2}(N_{\tau s}+1+\delta_\sigma^\tau)^{1/2}\alpha(s_{\sigma\tau}^{++}\boldsymbol{p}_{j\sigma\tau}^{--})e^{-i(\mu_\sigma+\mu_\tau)t} \\ &+ (N_{\sigma s}+1)^{1/2}(N_{\tau s}+\delta_\sigma^\tau)^{1/2}\alpha(s_{\sigma\tau}^{+-}\boldsymbol{p}_{j\sigma\tau}^{-+})e^{-i(\mu_\sigma-\mu_\tau)t} \\ &+ N_{\sigma s}{}^{1/2}(N_{\tau s}+1-\delta_\sigma^\tau)^{1/2}\alpha(s_{\sigma\tau}^{-+}\boldsymbol{p}_{j\sigma\tau}^{+-})e^{i(\mu_\sigma-\mu_\tau)t} \\ &+ N_{\sigma s}{}^{1/2}(N_{\tau s}-\delta_\sigma^\tau)^{1/2}\alpha(s_{\sigma\tau}^{--}\boldsymbol{p}_{j\sigma\tau}^{++})e^{i(\mu_\sigma+\mu_\tau)t}], \end{aligned} \tag{17}$$

in which such symbols as $s_\sigma{}^\pm$, $s_\sigma^{\pm\pm}$ refer to states the same as s except that N_σ and N_τ have been increased or decreased by unity as directed by the signs (or increased or decreased by 2 when $\sigma = \tau$), α being put equal to 0 when it thus comes to contain a negative N, $\delta_\sigma{}^\tau = 0$ except that $\delta_\sigma{}^\sigma = 1$, and

$$\boldsymbol{p}_{j\sigma}^{\pm} = \boldsymbol{p}_j \pm \gamma h\nu_\sigma\boldsymbol{n}_\sigma, \quad \boldsymbol{p}_{j\sigma\tau}^{\pm\pm} = \boldsymbol{p}_j \pm \gamma h\nu_\sigma\boldsymbol{n}_\sigma \pm \gamma h\nu_\tau\boldsymbol{n}_\tau. \tag{18}$$

It is to be understood that in a and α the $\boldsymbol{p}$'s of any particle not specifically indicated in the notation are the same throughout any given equation. In sums such as $\Sigma(\sigma, \tau)$ in (17) the terms $\sigma = \tau$ are a nuisance but they can fortunately usually be omitted in comparison with the other terms (i.e., their contribution comes out finally to be proportional to $\Delta\nu\Delta\omega$ and so vanishes in the limit).[5]

[5] A serious question as to the convergence of the sum in (17) arises if one really allows the range for ν_σ to extend to infinity, but all mathematical questions of this sort will be passed over in silence in this paper. Cf. L. Rosenfeld, Zeits. f. Physik **70**, 454 (1931).

Motion of Packet Centroids

A fundamental condition for the approximate validity of classical laws seems to be that we must be able to represent the particles by wave-packets which remain of negligible size over a considerable interval of time. The packets then move about practically like particles. Strictly speaking, only a single packet exists for the whole system, and it lies in a space whose coordinates include those of all particles and also all of the Q's; but we can fix our attention upon its location in the space of any single particle and regard it, seen from this angle, as a packet for that particle, and under classical conditions we can even imagine the virtual packets so obtained for the various particles all to move about in the same space. When the packets are small it suffices to consider the location and motion of their centroids; the laws of nature then take on their classical simplicity.

The vector coordinate of the jth particle being $\mathbf{x}_j$, the coordinate of its centroid is defined by

$$\bar{\mathbf{x}}_j = \int \mathbf{x}_j \psi^* \psi dq, \tag{19}$$

in which dq covers the Q's as well as the coordinates of all particles. The time derivatives of $\mathbf{x}_j$ are most easily obtained by the symbolic method,[6] which is easily extended to cover the present case by first deducing from the wave equation, Eq. (12), the "Hamiltonian equation of motion":

$$\begin{aligned}\frac{d}{dt}\int \psi^* f(x, \boldsymbol{p}, Q, P)\psi dq = \int \psi^* \Big\{ \sum(i)\Big[\Big(\frac{\partial f}{\partial x_i}\frac{\partial}{\partial p_i}\Big)W - \Big(\frac{\partial f}{\partial p_i}\frac{\partial}{\partial x_i}\Big)W\Big] \\ + \sum(\sigma)\Big[\Big(\frac{\partial f}{\partial Q_\sigma}\frac{\partial}{\partial P_\sigma}\Big)W - \Big(\frac{\partial f}{\partial P_\sigma}\frac{\partial}{\partial Q_\sigma}\Big)W\Big]\Big\}\psi dq.\end{aligned} \tag{20}$$

Here $\Sigma\,(i)$ extends over the coordinates of all particles and W is the Hamiltonian given by (7); a "compound" derivative such as $(\partial f/\partial x_i\,\partial/\partial p_i)W$ is to be calculated as in matrix theory by replacing in W each unit factor p_i^1 in turn by $\partial f/\partial p_i$ and adding the results, and, in both f and W, p_i and P_σ are to be treated as algebraic quantities except for the familiar interchange rules, $p_k x_l - x_l p_k = \epsilon\delta_k{}^l$, $P_\sigma Q_\tau - Q_\tau P_\sigma = \epsilon\delta_\sigma{}^\tau$, and are finally to be replaced by $\epsilon\partial/\partial x_i$, $\epsilon\partial/\partial Q_\sigma$ respectively just before carrying out the indicated integrations.

To find the centroid velocity for the jth particle we put each of its coordinates x_{jk} in turn for f in (20) and find, in vector notation,

$$\bar{\mathbf{v}}_j = \frac{d}{dt}\bar{\mathbf{x}}_j = \int \psi^*\Big(\frac{\epsilon}{m_j}\nabla_j - \frac{e_j}{cm_j}\sum(\sigma)\boldsymbol{b}_\sigma R_{\sigma j}\Big)\psi dq, \tag{21}$$

$R_{\sigma j}$ denoting R_σ with $x_{\sigma j}$ or $\boldsymbol{n}_\sigma \cdot \mathbf{x}_j$ substituted for x_σ. For the next differentiation we put for f, first, p_{jk}, then $R_{\sigma j} = R_{\sigma j}(x_j, Q, P)$, and obtain easily:

[6] Cf. E. H. Kennard, Nat. Acad. Sci. Proc. **17**, 58, (1931).

$$\epsilon d/dt \int \psi^* \nabla_j \psi dq = d/dt \int \psi^* \boldsymbol{p}_j \psi dq = (\boldsymbol{e}_j/2cm_j)$$

$$\int \psi^* \Big\{ [\boldsymbol{p}_j - \gamma e_j \sum(\sigma) \boldsymbol{b}_\sigma R_{\sigma j}] \cdot \sum(\tau) \boldsymbol{b}_\tau (\nabla_j R_{\tau j}) \tag{22}$$

$$+ \sum(\tau)(\nabla_j R_{\tau j}) \boldsymbol{b}_\tau \cdot [\boldsymbol{p}_j - \gamma e_j \sum(\sigma) \boldsymbol{b}_\sigma R_{\sigma j}] \Big\} \psi,$$

the dots denoting as usual the scalar vector product, and, after replacing $Q_\sigma \sin \gamma\mu_\sigma x_\sigma + P_\sigma \cos \gamma\mu_\sigma x_\sigma$, when met, by $-(\partial R_\sigma/\partial x_\sigma)/\gamma\mu_\sigma$,

$$d/dt \int \psi^* R_{\tau j} \psi dq = -c \int \psi^* (\partial R_{\tau j}/\partial x_{\tau j}) \psi dq$$

$$+ (1/2m_j) \int \psi^* \{ [\boldsymbol{p}_j - \gamma e_j \sum(\sigma) \boldsymbol{b}_\sigma R_{\sigma j}] \cdot (\nabla_j R_{\tau j})$$

$$+ (\nabla_j R_{\tau j}) \cdot [\boldsymbol{p}_j - \gamma e_j \sum(\sigma) \boldsymbol{b}_\sigma R_{\tau j}] \} \psi dq.$$

In both of these equations $(\nabla_j R_\tau)$ stands for $\boldsymbol{n}_\tau \, \partial R_\tau/\partial x_{\tau j}$, this ∇ not operating, as does the one below, on the following ψ. Upon substituting in $d\bar{\boldsymbol{v}}_j/dt$ as obtained by differentiating (21), the long integrals combine according to the vector formula for any vector $\boldsymbol{B}$, $\boldsymbol{B} \cdot \boldsymbol{b}_\tau (\nabla R) - \boldsymbol{B} \cdot (\nabla R_\tau) \boldsymbol{b}_\tau = \boldsymbol{B} \times [\nabla R_\tau \times \boldsymbol{b}_\tau] = \boldsymbol{B} \times (\boldsymbol{n}_\tau \times \boldsymbol{b}_\tau) \, \partial R_\tau/\partial x_\tau$. We may also consolidate the two terms occurring in each integral by means of the easily established interchange relations,

$$\boldsymbol{p}_j \frac{\partial R_{\tau j}}{\partial x_{\tau j}} - \frac{\partial R_{\tau j}}{\partial x_{\tau j}} \boldsymbol{p}_j = \epsilon \boldsymbol{n}_\tau \frac{\partial^2 R_{\tau j}}{\partial x_{\tau j}^2}, \quad R_{\sigma j} \frac{\partial R_{\tau j}}{\partial x_{\tau j}} - \frac{\partial R_{\tau j}}{\partial x_{\tau j}} R_{\tau j} = \epsilon \gamma \mu_\tau \delta_\sigma^\tau. \tag{23}$$

The final result thus obtained can be written:

$$\frac{d^2}{dt^2} \bar{\mathbf{x}}_j = \frac{e_j}{m_j} \int \psi^* \sum(\sigma) \boldsymbol{b}_\sigma \frac{\partial R_{\sigma j}}{\partial x_{\sigma j}} \psi dq$$

$$+ \frac{e_j}{cm_j} (Rl) \int \psi^* \left(\frac{\epsilon}{m_j} \nabla_j - \frac{e_j}{cm_j} \sum(\sigma) \boldsymbol{b}_\sigma R_{\sigma j} \right) \times \sum(\tau) \boldsymbol{n}_\tau \times \boldsymbol{b}_\tau \frac{\partial R_{\tau j}}{\partial x_{\tau j}} \psi dq, \tag{24}$$

where (Rl) means "real part only of what follows". The added terms arising from (23) have here been dropped because they are pure-imaginary, whereas $d^2\bar{\mathbf{x}}_j/dt^2$ must be real; the integrals multiplying ϵ in these dropped terms, like the first integral in (24), contain only real operators linear in P and Q and so are real (cf., e.g.,

$$I = \epsilon \int \psi^* \partial\psi/\partial Q \; dQ = \epsilon \psi^* \psi/ - \epsilon \int \psi \partial\psi^*/\partial Q dQ = I^* \Big).$$

Formulas (21) and (24) enable us to calculate the motion of all the packet centroids when ψ is known. They are strikingly similar in form to the formulas for a particle in an electromagnetic field expressed in the ordinary (but of course only approximately correct) manner; in fact the only difference is

that here the field vectors are replaced by the three operators, $\boldsymbol{A}=\Sigma(\sigma)\boldsymbol{b}_\sigma R_\sigma$, $\boldsymbol{E}=\Sigma(\sigma)\boldsymbol{b}_\sigma \partial R_\sigma/\partial x_\sigma$, $\boldsymbol{H}=\text{curl } \boldsymbol{A}=\Sigma(\sigma)\boldsymbol{n}_\sigma\times\boldsymbol{b}_\sigma\ \partial R_\sigma/\partial x_\sigma$, in which the coordinates of the particle under study are to be inserted. Each particle has, of course, its own electromagnetic field in its own space. One is tempted to form such averages as $\int\psi^*\Sigma(\sigma)\boldsymbol{b}_\sigma R_{\sigma j}\psi dq_{[j]}$, $dq_{[j]}$ covering all coordinates except those of one particle, and then to treat these quantities as field vectors in the space of that particle; if we leave the particle out of consideration altogether these vectors are indeed easily shown to satisfy the Maxwell equations, but with the particle present one is led to very complicated expressions.

For some purposes, on the other hand, we need an alternative form of these expressions in terms of the harmonic constituents of the wave-function. Such forms are readily obtained by inserting ψ from (14) into (21) and (24) and evaluating the integrals in the same way as in arriving at (17). One thus finds for the jth particle:

$$\overline{\boldsymbol{A}_j} = (h/4\pi)^{1/2}\sum(s)\int dp\ \sum(\sigma)\boldsymbol{b}_\sigma[(N_{\sigma s}+1)^{1/2}\alpha^*(s\overset{+}{\sigma}\boldsymbol{p}\overset{-}{j\sigma})e^{i\mu_\sigma t} + N_{\sigma s}{}^{1/2}\alpha^*(s\overset{-}{\sigma}\boldsymbol{p}\overset{+}{j\sigma})e^{-i\mu_\sigma t}]\alpha(s\boldsymbol{p}), \quad (25)$$

$$d\mathbf{x}_j/dt = (1/m_j)\ \sum(s)\int \boldsymbol{p}_j\alpha^*(s\boldsymbol{p})\alpha(s\boldsymbol{p})dp - e_j\overline{\boldsymbol{A}}_j/cm_j, \quad (26)$$

$$\begin{aligned} d^2\overline{\mathbf{x}}_j/dt = &-(ie_j/cm_j)(\pi h)^{1/2}\ \sum(s)\int dp\sum(\sigma)\nu_\sigma[\boldsymbol{b}_\sigma+(1/cm_j)\boldsymbol{p}_j\times(\boldsymbol{n}_\sigma\times\boldsymbol{b}_\sigma)] \\ &[(N_{\sigma s}+1)^{1/2}\alpha^*(s\overset{+}{\sigma}\boldsymbol{p}\overset{-}{j\sigma})e^{i\mu_\sigma t} - N_{\sigma s}{}^{1/2}\alpha^*(s\overset{-}{\sigma}\boldsymbol{p}\overset{+}{\sigma j})e^{-i\mu_\sigma t}]\alpha(s\boldsymbol{p}) \\ &+(ie_j{}^2h/2c^3m_j{}^2)\ \sum(s)\int dp\ \sum(\sigma\tau)\nu_\tau\boldsymbol{b}_\sigma\times(\boldsymbol{n}_\tau\times\boldsymbol{b}_\tau) \\ &\{[(N_{\sigma s}+1)(N_{\tau s}+1+\delta_\sigma{}^\tau)]^{1/2}\alpha^*(s\overset{++}{\sigma\tau}\boldsymbol{p}\overset{--}{j\sigma\tau})e^{i(\mu_\sigma+\mu_\tau)t} \\ &+[(N_{\sigma s}+1)(N_{\tau s}+\delta_\sigma{}^\tau)]^{1/2}\alpha^*(s\overset{+-}{\sigma\tau}\boldsymbol{p}\overset{-+}{j\sigma\tau})e^{i(\mu_\sigma-\mu_\tau)t} \\ &-[N_{\sigma s}(N_{\tau s}+1-\delta_\sigma{}^\tau)]^{1/2}\alpha^*(s\overset{-+}{\sigma\tau}\boldsymbol{p}\overset{+-}{j\sigma\tau})e^{-i(\mu_\sigma-\mu_\tau)t} \\ &-[N_{\sigma s}(N_{\tau s}-\delta_\sigma{}^\tau)]^{1/2}\alpha^*(s\overset{--}{\sigma\tau}\boldsymbol{p}\overset{++}{j\sigma\tau})e^{-i(\mu_\sigma+\mu_\tau)t}\}\alpha(s\boldsymbol{p}), \end{aligned} \quad (27)$$

the notation being as in (17). The evaluation of sums such as occur here is apt to be a tedious process, but the work can often be halved by noting that the contributions of any given pair of field-states to $\Sigma(s)\int dp$ in these formulas are merely complex conjugates of each other.

It is noteworthy that with respect to all of these formulas the quantum-states of the particle-field system, represented by the various pairs of values of s and $\boldsymbol{p}$, fall into an infinite number of non-combining groups, each characterized by a certain value of the total momentum, $\Sigma(j)\boldsymbol{p}_j+\Sigma(\sigma)\gamma h\nu_\sigma\boldsymbol{n}_\sigma$. It is well known that only states belonging to the same one of these "Compton" groups influence each other's amplitudes, as shown by (17); for this reason in problems on energy or momentum only a single typical group has usually been employed, represented by a single initial state for the field. But it appears like-

wise from (25) to (27) that only members of the same group combine with each other in producing packet motion, so that many features of this motion, too, can be obtained from the study of one group alone. On the other hand, since concentration in space requires that for any given field state the packet must extend over an appreciable range in $\boldsymbol{p}$, there will be other features which depend essentially upon the co-existence of many different Compton groups. As a matter of fact, in radiation problems the use of a single group has always compelled the resort to a special device of some sort in order to make connection with the spatial intensity of the radiation.

If the field is in any single pure quantum state (e.g., $\alpha(s\boldsymbol{p})=0$ except when $s=s_1$), then it is obvious from (25), (26) and (27) that it has no direct effect upon the motion of the centroid. There may, however, be an indirect effect through values of the α's arising from interaction with the test particle; unfortunately this question, involving the field close to the particle that emits it, lies beyond the reach of the present analysis. In the special case of a particle at rest with the field in the normal or lowest-energy state, however, it is clear from symmetry considerations that the acceleration of the packet centroid must really vanish. This is very satisfactory because it means that the "infinite energy" $\Sigma(\sigma)h\nu_\sigma/2$ associated with this state, whatever its true significance, at least implies no observable electromagnetic field. On the other hand, if one wave-train is "excited" (one $N_{\sigma s}$ not zero), there must be a steady forward acceleration of the packet corresponding to the mean Compton recoil and representing an elementary sort of radiation pressure upon the particle; it seems impossible, however, that the acceleration should include any component oscillating with frequency ν_σ, for there is nothing in the situation to fix the phase of such an oscillation. In this case we have an elementary sort of radiation pressure but in the ordinary sense no electric or magnetic intensity.

These pure quantum states of the field represent, of course, ideal conditions that never actually occur. But the same situation should obtain even with the field in a mixed state whenever the initial spread in the momentum $\boldsymbol{p}$ is small compared to the Compton kicks, of magnitude $h\nu_\sigma/c$, associated with all wave-trains that can contribute appreciably to the centroid motion, as is the case in observations on the Compton effect; for then in each product of two α's in the formulas one factor or the other contains a value of $\boldsymbol{p}$ lying outside the initial range and so vanishes approximately.

The ordinary null-field representing the absence of all radiation, which we always take as a starting point in emission problems, cannot, however, be assumed to correspond to the field's being entirely in its quantum state of lowest energy, for from (17) it is obvious that the presence of charged particles, even if unaccelerated, will not leave the field in this state. The null-field appears to be one containing many different quantum states with amplitudes that are completely disorganized. Such a lack of organization, arising eventually from the various time-factors in (17), prevents the existence of any correlation between the α's that come to be multiplied together in (25) and (27), so that positive and negative values cancel each other on the whole, i.e., we

have complete destructive interference among the wave-trains, and the net physical effect is nil.

A physical wave-train must likewise be represented by a combination of field states, only in this case there is a certain type of coordination among their coefficients. Of this an example is obtained in the next section.

The Classical Case

We are now ready to attack the principal problem of the present paper, namely, the manner in which the quantum theory of radiation passes over under suitable conditions into classical theory as a first approximation.

The classical case, as stated above, is one in which the particles can be represented by wave-packets that preserve a certain particle-like character for a considerable length of time. To avoid disrupting them it appears that the radiation field must be sufficiently coarse-grained to be approximately uniform over the wave-packet for each particle; that is, if Δx is the effective diameter of the packet and λ the wave-length of the radiation, we must have $\Delta x/\lambda \ll 1$. At the same time the spread of momentum Δp must of course satisfy the relation of indetermination, $\Delta x \Delta p > h$ (roughly). Now such a spread of momentum tends, as time goes on, to blur the packet; we may say roughly that the diameter will increase at a rate $\Delta v = \Delta p/m$ and so will become equal to λ in a time $\lambda m/\Delta p$. During this time we shall want to follow the particle during at least several oscillations under the influence of the field. Hence we shall want to have $(\lambda m/\Delta p)v = mc/\Delta p \gg 1$, a condition that is easy to satisfy at ordinary speeds. By multiplication of these three inequalities we can obtain others; combining two of the latter with the first one above, we can write as an expression for the relation of indetermination and the conditions for the classical case combined:

$$\Delta x/\lambda \ll 1,\ h\nu/(c\Delta p) \ll 1,\ \lambda \gg h/mc. \tag{28}$$

The second of these inequalities can be interpreted as meaning that the maximum Compton kick due to the field, $h\nu/c$, must be much less than the indefiniteness in momentum; thus it is characteristic of the classical case that the Compton effect is reduced to a slight blurring of the packet which is quite negligible as compared with the effect of the natural degree of indefiniteness in the velocity. The third inequality, on the other hand, sets an actual limit to the smallness of the scale upon which anything like a classical relation between radiation and motion can hold at all. Characteristic quantum phenomena are possible under suitable conditions upon any scale; for instance, in principle the Compton effect might be observed with free electrons and Hertzian waves, the electrons being so closely controlled in velocity for this purpose that their position would be indefinite by miles. On such large scales phenomena may be either approximately classical or more or less quantum-mechanical in character, depending upon conditions. But below the limit of size set by the third inequality above radiation phenomena are bound to present more or less of a non-classical aspect.

Let us now fix our attention upon the radiation emitted by a particle of

charge e, mass m, and coordinates $\boldsymbol{x}$ and $\boldsymbol{p}$, as detected by its effect upon a second particle for which corresponding quantities are e', m', $\boldsymbol{x}'$, $\boldsymbol{p}'$. To make the first particle radiate we must subject it to an accelerating force, and to preserve classical conditions this force must likewise be practically uniform over the packet; we shall represent it by a potential energy term $V = -\boldsymbol{g}(t)\cdot x$. The complete wave-equation will then be

$$-\epsilon\frac{\partial\psi}{\partial t} = \sum(\sigma)\pi\nu_\sigma\left(Q_\sigma^2 + \epsilon^2\frac{\partial^2}{\partial O_\sigma^2}\right)\psi + (1/2m)(\epsilon\nabla - \gamma e\sum(\sigma)\boldsymbol{b}_\sigma R_\sigma)^2\psi$$
$$+ (1/2m')(\epsilon\nabla' - \gamma e'\sum(\sigma)\boldsymbol{b}_\sigma R_\sigma')^2\psi - \boldsymbol{g}\cdot\boldsymbol{x}\psi, \tag{29}$$

the primes on ∇' and R' indicating that $\boldsymbol{x}'$ in place of $\boldsymbol{x}$ occurs in these operators.

To allow, first, for the effect of V, consider the simpler case:

$$-\epsilon\partial\psi/\partial t = (\epsilon^2/2m)\nabla^2\psi + (\epsilon^2/2m')\nabla'^2\psi - \boldsymbol{g}\cdot\boldsymbol{x}\psi,\ \psi = \int\alpha(\boldsymbol{pp}')e^{\zeta(\boldsymbol{p}\cdot\boldsymbol{x}+\boldsymbol{p}'\cdot\boldsymbol{x}')}dpdp'.$$

One easily verifies that

$$\alpha(\boldsymbol{p}') = \alpha_0(\boldsymbol{p} - \boldsymbol{G}_t, \boldsymbol{p}')e^{\zeta\eta},\quad \boldsymbol{G}_t = \int_0^t \boldsymbol{g}dt,$$
$$\eta = -p'^2t/2m' + (1/2m)\left[-p^2t + 2\boldsymbol{p}\cdot\left(\boldsymbol{G}t - \int_0^t \boldsymbol{G}_t dt\right)\right. \tag{30}$$
$$\left. -2\int_0^t dt\ \ \boldsymbol{g}\cdot\int_0^t \boldsymbol{g}'(t_2)t_2dt_2\right],$$

is a solution reducing to $\alpha=\alpha_0$ at $t=0$ (the term $\boldsymbol{g}\cdot\boldsymbol{x}\psi$ arising in the wave-equation from an integration by parts in p); we have thus for the rate of change of α,

$$\dot\alpha = (0\dot p)\alpha = -\zeta(p^2/2m + p'^2/2m')\alpha - \boldsymbol{g}\cdot\nabla_p\alpha, \tag{31}$$

∇_p denoting a vector whose components are $\partial\alpha/\partial p_k$. The quantity $\boldsymbol{G}_t$ represents, of course, the total change in the mean expectation of momentum, $\bar{\boldsymbol{p}} = \int\boldsymbol{p}\alpha^*\alpha\,dp$, during the time t.

Returning now to the general case, let us write

$$\psi = h^{-3}\sum(s)\iint\alpha(s\boldsymbol{pp}')e^{\zeta(\boldsymbol{p}\cdot\boldsymbol{x}+\boldsymbol{p}'\cdot\boldsymbol{x}'-W_{s'})}dpdp'. \tag{32}$$

For the present, however, we shall assume that initially only one field state is present, that is, $\alpha(s\boldsymbol{pp}')$ differs from zero only for one chosen value of s and $\iint\alpha^*(s\boldsymbol{pp}')\alpha(s\boldsymbol{pp}')dpdp' = 1$; and in order to restrict our calculation to radiation by the first particle alone we shall consider only the wisps of side-terms that arise out of this initial state through the influence of the first particle as expressed by its term in the Hamiltonian. Adding the g-effect out of (31) in (17), in which we now add $\boldsymbol{p}'$ as a new variable in all α's, we find:

$$\dot{\alpha}(s_\sigma^{\pm}\boldsymbol{p}\boldsymbol{p}') = (Op)\alpha(s_\sigma^{\pm}\boldsymbol{p}\boldsymbol{p}') + (e\zeta/cm)(h/4\pi)^{1/2}(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}\boldsymbol{b}_\sigma\cdot\boldsymbol{p}\alpha(s\boldsymbol{p}_\sigma^{\pm}\boldsymbol{p}')e^{\pm i\mu_\sigma t},$$

$$\dot{\alpha}(s_{\sigma\tau}^{\pm\pm}\boldsymbol{p}\boldsymbol{p}') = (Op)\alpha(s_{\sigma\tau}^{\pm\pm}\boldsymbol{p}\boldsymbol{p}') - (ie^2/4c^2m)[(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})(N_{\tau s}+\tfrac{1}{2}\pm\tfrac{1}{2})]^{1/2}\boldsymbol{b}_\sigma\cdot\boldsymbol{b}_\tau\alpha(s\boldsymbol{p}_{\sigma\tau}^{\pm\pm}\boldsymbol{p}')e^{i(\pm\mu_\sigma\pm\mu_\tau)t}, \quad (33b)$$

the latter valid only for $\sigma\neq\tau$. For $\sigma=\tau$ we get such equations as

$$\dot{\alpha}(s\boldsymbol{p}\boldsymbol{p}') = (Op)\alpha(s\boldsymbol{p}\boldsymbol{p}') - (ie^2/4c^2m)\sum(\sigma)(2N_{\sigma s}+1)\boldsymbol{b}_\sigma^2\alpha(s\boldsymbol{p}\boldsymbol{p}'),$$

in which the last term is enormous but after all merely serves to rotate α at high speed in the complex plane; the same sort of rotating term really should appear in all of the $\dot{\alpha}$'s, except for changes in one or two $N_{\sigma s}$'s whose effect vanishes with $\Delta\nu\Delta\omega$, hence this rotation will be without physical effect in the end, and we shall accordingly ignore it from this point on. All other $\dot{\alpha}$'s are zero. Accordingly, by (31) and (30),

$$\alpha(s\boldsymbol{p}\boldsymbol{p}') = \alpha_0(s, \boldsymbol{p}-\boldsymbol{G}_t, \boldsymbol{p}')e^{\zeta\eta}. \quad (34)$$

Upon substituting this value of α in the last term in (33a,b) we get, since $\boldsymbol{b}_\sigma\cdot\boldsymbol{p}=\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_\sigma^{\pm}=\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_{\sigma\tau}^{\pm\pm}$, equations of the type,

$$\dot{\alpha} = (Op)\alpha + \alpha(s\boldsymbol{p}\boldsymbol{p}')F(\boldsymbol{p}, t),$$

whose solution vanishing at $t=0$ is

$$\alpha = \alpha(s\boldsymbol{p}\boldsymbol{p}')\int_0^t F(\boldsymbol{p}-\boldsymbol{G}_t+\boldsymbol{G}_{t_1}, t_1)dt_1.$$

We thus find:

$$\alpha(s_\sigma^{\pm}\boldsymbol{p}\boldsymbol{p}') = (e\zeta/cm)(h/4\pi)^{1/2}(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}\alpha(s\boldsymbol{p}_\sigma^{\pm}\boldsymbol{p}')\int_0^t \boldsymbol{b}_\sigma\cdot(\boldsymbol{p}-\boldsymbol{G}_t+\boldsymbol{G}_{t_1})e^{\pm i\mu_\sigma t_1}dt_1, \quad (35)$$

$$\alpha(s_{\sigma\tau}^{\pm\pm}\boldsymbol{p}\boldsymbol{p}') = -(ie^2/4c^2m)[(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})(N_{\tau s}+\tfrac{1}{2}\pm\tfrac{1}{2})]^{1/2}\boldsymbol{b}_\sigma\cdot\boldsymbol{b}_\tau\alpha(s\boldsymbol{p}_{\sigma\tau}^{\pm\pm}\boldsymbol{p}')\int_0^t e^{i(\pm\mu_\sigma\pm\mu_\tau)t_1}dt_1, \quad (36)$$

in which all α's denote values at time t and the second equation holds only for $\sigma\neq\tau$.

We now direct our attention to the second particle and find in its space the mean vector potential due to the radiation field emitted by the first particle as represented by (34), (35) and (36). In Eq. (25) we replace the subscript j by a prime throughout and add $\boldsymbol{p}$ as another variable in all α's; the sums $\Sigma(s)\Sigma(\sigma)$ reduce to two sets of terms, one set in which our chosen initial $\alpha(s\boldsymbol{p}\boldsymbol{p}')$ functions as $\alpha(s\boldsymbol{p}\boldsymbol{p}')$ in (25) and the values of α given by (35) as the α's in the bracket, and a second set, complex conjugates of the first, in which

these roles are reversed. The values of α given by (36) yield nothing appreciable. Putting

$$\boldsymbol{p} - \boldsymbol{G}_t + \boldsymbol{G}_{t_1} = \boldsymbol{p}_1,$$

the result can be written:

$$\overline{\boldsymbol{A}'} = -(ie/2cm)\int\int dpdp' \sum(\sigma)\boldsymbol{b}_\sigma e^{i\mu_\sigma t}[(N_{\sigma s}+1)\alpha^*(s\overset{+}{\boldsymbol{p}}_\sigma\boldsymbol{p}_\sigma'^-)\alpha(s\boldsymbol{p}\boldsymbol{p}') - N_{\sigma s}\alpha^*(s\boldsymbol{p}\boldsymbol{p}_\sigma'^-)\alpha(s\bar{\boldsymbol{p}}_\sigma\bar{\boldsymbol{p}}')]\int_0^t \boldsymbol{b}_\sigma'\cdot\boldsymbol{p}_1 e^{-i\mu_\sigma t_1}dt_1 + \text{conjugate}. \tag{37}$$

In $\boldsymbol{p}_1$ we should have, according to (25), $\boldsymbol{p}_\sigma^\pm$ in place of $\boldsymbol{p}$, but this is immaterial because $\boldsymbol{b}_\sigma\cdot(\boldsymbol{p}_\sigma^\pm-\boldsymbol{p}) = \pm\gamma h\nu_\sigma\boldsymbol{b}_\sigma\cdot\boldsymbol{n}_\sigma = 0$.

The p and p' integrations may now be carried out first; this requires a bit of packet theory which can be indicated in sufficient detail as follows. Assuming that only the one state s contributes appreciably to the integrals, one easily finds, after a partial integration or two in one set of p's,

$$\bar{\mathbf{x}} = \int \mathbf{x}\psi^*\psi dq = -\epsilon\int\int \alpha^*\nabla_p\alpha dpdp',$$

$$(av)(\mathbf{x}-\bar{\mathbf{x}})^2 \equiv \int(\mathbf{x}-\bar{\mathbf{x}})^2\psi^*\psi dq = \frac{h^2}{4\pi^2}\int\int|\nabla_p\alpha|^2 dpdp' - \bar{\mathbf{x}}^2;$$

whereas if we introduce the centroid explicitly by writing $\alpha = \beta e^{-i\boldsymbol{p}\cdot\bar{\mathbf{x}}}$,

$$\int\int\beta^*\nabla_p\beta dpdp' = 0, \quad D^2 \equiv (av)(\mathbf{x}-\bar{\mathbf{x}})^2 = \frac{h^2}{4\pi^2}\int\int|\nabla_p\beta|^2 dpdp'. \tag{38}$$

Similar formulas hold for the second particle as well. The Compton shift of $\boldsymbol{p}$ in the factor $e^{-i\boldsymbol{p}\cdot\bar{\mathbf{x}}}$ serves to introduce into the result the location of the particles. The occurrence of the same shift in β, on the other hand, is unimportant under our conditions. For the difference between such an integral as $\int\int\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1\beta^*(\boldsymbol{p}_\sigma^\pm)\beta(\boldsymbol{p})dpdp'$ and $(av)\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1 \equiv \int\int\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1\beta^*(\boldsymbol{p})\beta(\boldsymbol{p})dpdp'$ should be of the order of $\left|\int\int\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1\gamma h\nu_\sigma|\nabla_p\beta||\beta|dpdp'\right|$, which, since the spread of momentum is small in the quasi-classical case and $\boldsymbol{b}_\sigma$ is a constant, is nearly the same as $\gamma h\nu_\sigma[(av)\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1]\int\int|\beta\nabla_p\beta|dpdp'$, and by the Schwarz inequality the square of the latter integral cannot exceed $\int\int|\beta|^2dpdp'\int\int|\nabla_p\beta|^2dpdp' = \int\int|\nabla_p\beta|^2dpdp' = 4\pi^2D^2/h^2$ by (38). Thus the original difference is of order $2\pi D[(av)\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1]/\lambda_\sigma$ and so is small compared with $(av)\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1$ itself by the first of the inequalities (28). A rigorous treatment of the matter is readily constructed, with further use of the Schwarz inequality, but it is devoid of physical interest and will be omitted.

Accordingly, writing

$$\alpha(s\boldsymbol{p}\boldsymbol{p}') = \beta(s\boldsymbol{p}\boldsymbol{p}')e^{-i(\boldsymbol{p}\cdot\bar{\mathbf{x}}+\boldsymbol{p}'\cdot\bar{\mathbf{x}}')} \tag{39}$$

and $\bar{\boldsymbol{p}}_1 = \int\int\boldsymbol{p}_1\beta^*(s\boldsymbol{p}\boldsymbol{p}')\beta(s\boldsymbol{p}\boldsymbol{p}')dpdp'$, where $\bar{\boldsymbol{p}}_1 = \bar{\boldsymbol{p}} - G_t + G_{t_1}$ and so represents the value of $\bar{\boldsymbol{p}}$, the average momentum, at time t_1, (37) becomes:

$$\overline{\boldsymbol{A}'} = -(ie/2cm)\sum(\sigma)\boldsymbol{b}_\sigma e^{i\mu_\sigma(t+\gamma\boldsymbol{n}_\sigma\cdot\bar{\boldsymbol{x}}-\gamma\boldsymbol{n}_\sigma\cdot\bar{\boldsymbol{x}}')}\int \boldsymbol{b}_\sigma\cdot\bar{\boldsymbol{p}}_1 e^{-i\mu_\sigma t_1}dt_1 + \text{conjugate}$$

or

$$\overline{\boldsymbol{A}'} = (e/cm)\sum(\sigma)\boldsymbol{b}_\sigma \quad \boldsymbol{b}_\sigma\cdot\int_0^t \bar{\boldsymbol{p}}_1 \sin\mu_\sigma(t+\gamma\bar{x}_\sigma-\gamma\bar{x}_\sigma'-t_1)dt_1. \qquad (40)$$

This expression agrees with that in (9) except that $\bar{\boldsymbol{p}}_1/m$ replaces $\boldsymbol{v}$ and the two sets of centroid coordinates replace those of the radiating particle and of the field point respectively. We thus obtain finally the classical expression, (12), for $\boldsymbol{A}$, with $\bar{\boldsymbol{p}}_1/m$ replacing $\boldsymbol{v}$ throughout; the first particle affects the second approximately as if they were classical particles following their respective packet centroids.

The calculation just given is readily generalized to cover the initial presence of more than one field state. The only cases of this sort which are of interest in the present connection are two in which a great many states occur with certain relations as to amplitude and phase. On the one hand, the amplitudes may be entirely disorganized, representing a physical null-field. Then combinations between each of the initial states and the side-terms arising out of the others will destroy each other by interference; each initial state will yield a contribution to $\overline{\boldsymbol{A}}$ like that just obtained but multiplied by the probability of the state, $k_s^2=\iint|\alpha(s\boldsymbol{p}\boldsymbol{p}')|^2 dpdp'$, and the total result for emission by a particle will come out as before. On the other hand, the various states may be so correlated in amplitude that they represent in the space of the radiating particle a vector potential $\boldsymbol{A}_0$ coming from other sources. In the latter case intercombinations between each of these initial states and the side-terms arising out of the others serve to introduce into the radiation from our particle the component arising from a term, $-e\boldsymbol{A}_0/cm$, in its velocity; but we shall give no further details.

The results just obtained constitute, unfortunately, only a partial deduction of the classical law, since the law of force, Eq. (24), has not the usual form in terms of derivatives of $\boldsymbol{A}$. Apparently it is necessary to show directly that (24) or (27) leads also, under our conditions, to the familiar formula, $m\ddot{\boldsymbol{x}}=e\boldsymbol{E}+e\boldsymbol{v}\times\boldsymbol{H}/c$. This is in fact not hard to do, but we shall indicate the details only for the most difficult term, the last one in (24) or the e_j^2 term in (27), representing the combined effect of the velocity due to the vector potential and the magnetic field of the same physical wave-train. This term contains the average of the product $\boldsymbol{A}\times\boldsymbol{H}$, but such an expression cannot in general be separated into the product of the averages, $\overline{\boldsymbol{A}}\times\overline{\boldsymbol{H}}$.

To evaluate this quadratic term it turns out that we have to go to the second approximation for the values of α. We have here a characteristic difference between classical and quantum mechanics, for in classical theory the values of the P's and Q's are obtained once for all in terms of other quantities (Eq. (8a) above). As a matter of fact, contrary to first appearances, a given $\alpha(s)$ does not correspond to an assignment in classical theory of the amplitude of each P and Q; it has reference to a more fundamental wave-oscillation de-

void of any classical analogue whatever. A set of amplitudes of the classical P's and Q's corresponds to a wave-packet for the field consisting of many $\alpha(s)$'s in combination. Thus Eqs. (35) and (36) do not really correspond at all to the classical Eqs. (8a).

To obtain the second approximation we insert the values of $\alpha(s_\tau{}^{\pm}pp')$ as given by (35) for $\alpha(spp')$ on the right of (33a), repeat with σ changed to τ in (33a) instead of in (35), and, adding the results, obtain $\dot{\alpha}(s_{\sigma\tau}{}^{\pm\pm}pp')$; from this $\alpha(s_{\sigma\tau}{}^{\pm\pm}pp')$ can at once be written down just as in obtaining (35) from (33a). The resulting two double integrals with respect to t fit together into one, thus:

$$\int_0^t \boldsymbol{b}_\sigma\cdot\boldsymbol{p}_2 e^{\pm i\mu_\sigma t_2}dt_2\int_0^{t_2}\boldsymbol{b}_\tau\cdot\boldsymbol{p}_1 e^{\pm i\mu_\tau t_1}dt_1+\int_0^t \boldsymbol{b}_\tau\cdot\boldsymbol{p}_2 e^{\pm i\mu_\tau t_2}dt_2\int_0^{t_2}\boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1 e^{\pm i\mu_\sigma t_1}dt_1$$
$$=\int_0^t dt_1\int_0^t \boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1\boldsymbol{b}_\tau\cdot\boldsymbol{p}_2 e^{\pm i\mu_\sigma t_1\pm i\mu_\tau t_2}dt_2.$$

Accordingly

$$\alpha(s_{\sigma\tau}^{\pm\pm}\boldsymbol{p}\boldsymbol{p}') = -(\pi e^2/c^2m^2h)(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}(N_{\tau s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}$$
$$\alpha(s\boldsymbol{p}_{\sigma\tau}^{\pm\pm})\int_0^t \boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1 e^{\pm i\mu_\sigma t_1}dt_1\int_0^t \boldsymbol{b}_\tau\cdot\boldsymbol{p}_1 e^{\pm i\mu_\tau t_1}dt_1. \quad (41)$$

We now go to Eq. (27), replace in it the subscript j by a prime and add p as a variable in α, and then substitute for the α's in the e'^2 term on the right $\alpha(spp')$, $\alpha(s_\sigma{}^{\pm}pp')$ from (35), and $\alpha(s_{\sigma\tau}{}^{\pm\pm}pp')$ from (41). Most of the terms in $\Sigma(s)\Sigma(\sigma,\tau)$ vanish, but the two series of values $\alpha(s_\sigma{}^{+})$ and $\alpha(s_\sigma{}^{-})$ combine with each other and with themselves, and $\alpha(s)$ combines with $\alpha(s_{\sigma\tau}{}^{\pm\pm})$. The sixteen expressions thus found we shall not write down; we shall merely state that, after the $\boldsymbol{p}$ shifts have been replaced by centroid factors as was done in calculating $\boldsymbol{A}$, the terms all combine up very nicely and give us for the e'^2 term in (27):

$$(e'/cm')\iint|\beta(s\boldsymbol{p}\boldsymbol{p}')|^2 dpdp'(-e'/cm')$$
$$\left[(e/cm)\sum(\sigma)\boldsymbol{b}_\sigma\int_0^t \boldsymbol{b}_\sigma\cdot\boldsymbol{p}_1\sin\mu_\sigma(t+\gamma\bar{x}_\sigma-\gamma\bar{x}_\sigma'-t_1)dt_1\right]$$
$$\times\left[(-2\pi e/c^2m)\sum(\tau)\nu_\tau\boldsymbol{n}_\tau x\boldsymbol{b}_\tau\int_0^t \boldsymbol{b}_\tau\cdot\boldsymbol{p}_1\cos\mu_\tau(t+\gamma\bar{x}_\tau-\gamma\bar{x}_\tau'-t_1)dt_1\right].$$

Comparison with (40) then shows that the first square bracket represents the vector potential emitted by a particle with momentum $\bar{\boldsymbol{p}}_1$, while the second bracket is the curl of this potential taken with respect to the coordinates of the second particle, since curl $[\boldsymbol{b}_\tau f(\bar{x}_\tau')]=\nabla f(\bar{x}_\tau')\times\boldsymbol{b}_\tau=\boldsymbol{n}_\tau\partial f/\partial\bar{x}_\tau'\times\boldsymbol{b}_\tau$. The whole expression thus represents the expected classical component of acceleration, $(e'/cm')(-e'\boldsymbol{A}/cm')\times\boldsymbol{H}=e\boldsymbol{v}_A\times\boldsymbol{H}/cm$, averaged for all momentum constituents of the radiating packet just as if each of these radiated its own com-

plete field. Since this packet was supposed to be very concentrated in momentum we have thus the classical result.

The waves obtained above are diverging spherical waves, but of course by removing the radiating particle to infinity they can be converted into plane waves. In classical theory such waves can also be obtained more simply merely by assuming just one pair of the Q's and P's to differ from zero by a finite amount. The expression obtained in the latter way is, however, really of the nature of a singular solution; it is not the limiting form of (9) above; and in quantum theory it seems to possess no true analogue.

Apparently the simplest adequate representation of a plane train is the following. Introducing the centroids into (35) and (41) as before by means of (39), let us drop out of the factor, $\exp(-\zeta \boldsymbol{p}\cdot\bar{\mathbf{x}})$, the part that merely cancels in the end and retain only $\exp[-\zeta(\boldsymbol{p}_\sigma{}^{\pm}-\boldsymbol{p})\cdot\bar{\mathbf{x}}]=\exp[\mp i\mu_\sigma\gamma\bar{x}_\sigma]$ and the similar expression in both σ and τ. As the emitting particle recedes to infinity let its charge e increase in proportion to its distance; we then drop it from view as a particle by ignoring $\boldsymbol{p}$ in β, where it merely serves to average over the packet, and writing $-\rho\boldsymbol{n}$ for $\mathbf{x}$, in which we now regard ρ merely as a large number with the dimensions of distance and $\boldsymbol{n}$ as a unit vector. For $\boldsymbol{p}-\boldsymbol{G}_t+\boldsymbol{G}_{t1}=\boldsymbol{p}_1$ let us write $C_1\boldsymbol{l}\cos\mu_0 t_1$; the integrals are then easily evaluated. Omitting, finally, the factors referring explicitly to the second particle, we find in this way from (35) and (41) as the representation of a plane wave-train of frequency $\nu_0=\mu_0/2\pi$, with electric vector in the direction $\boldsymbol{l}$ and ray-direction $\boldsymbol{n}$, the following coordinated set of field states:

$$\alpha(s) = k$$

$$\alpha(s_\sigma^{\pm}) = \frac{\rho C}{2}\left(\frac{\mu_\sigma\Delta\nu\Delta\omega}{ch}\right)^{1/2}(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}\boldsymbol{l}\cdot\boldsymbol{l}_\sigma e^{\pm i\gamma\rho\mu_\sigma\boldsymbol{n}\cdot\boldsymbol{n}_\sigma}\left[\frac{e^{i(\mu_0\pm\mu_\sigma)t}-1}{\mu_0\pm\mu_\sigma}+\frac{e^{i(-\mu_0\pm\mu_\sigma)t}-1}{-\mu_0\pm\mu_\sigma}\right] \quad (42)$$

$$\alpha(s_{\sigma\tau}^{\pm\pm}) = \frac{\rho^2C^2}{4}\frac{\mu_\sigma\Delta\nu\Delta\omega}{ch}(N_{\sigma s}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}(N_{\sigma\tau}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}\boldsymbol{l}\cdot\boldsymbol{l}_\sigma\boldsymbol{l}\cdot\boldsymbol{l}_\tau$$

$$e^{i\gamma\rho\boldsymbol{n}\cdot(\pm\mu_\sigma\boldsymbol{n}_\sigma\pm\mu_\tau\boldsymbol{n}_\tau)}\left[\frac{e^{i(\mu_0\pm\mu_\sigma)t}-1}{\mu_0\pm\mu_0}+\frac{e^{i(-\mu_0\pm\mu_\sigma)t}-1}{-\mu_0\pm\mu_\sigma}\right]\left[\frac{e^{i(\mu_0\pm\mu_\tau)t}-1}{\mu_0\pm\mu_\tau}+\frac{e^{i(-\mu_0\pm\mu_\tau)t}-1}{-\mu_0\pm\mu_\tau}\right]$$

in which ρ is to be made infinite at the end, $C=eC_1/cm\rho$ and is arbitrary, and k is another arbitrary constant that we have introduced for generality; σ and τ are to take on all positive values. The corresponding vector potential for a particle placed in the field with coordinate $\mathbf{x}$ is, from (11), in which we replace $\boldsymbol{v}_\perp(t)$ by $k\boldsymbol{p}_{1\perp}/m$ and then $\boldsymbol{p}_{1\perp}$ by $C_1\boldsymbol{l}\cos\mu_0 t$, assume γv_r negligible, drop the last term as likewise negligible, put $r=\rho+\boldsymbol{n}\cdot\mathbf{x}$, and then let $\rho\to\infty$:

$$\boldsymbol{A} = kC\boldsymbol{l}\cos\mu_0(t-\gamma\boldsymbol{n}\cdot\mathbf{x}-t_0).$$

The intensity of the beam (Poynting's vector) is $\pi\nu_0^2k^2C^2/2c$.

If in Eqs. (42) we put $s=0$ and take it to refer to the "normal" state of the field ($N_{\sigma s}=0$), then only states of the type 0, $0_\sigma{}^+$ and $0_{\sigma\tau}{}^{++}$ occur. This simple

case is really adequate for the treatment of all practical problems; in the present paper the mere general case of any initial state was preferred merely as a matter of theoretical interest. For problems in energy or momentum one may then, as is usual, simplify the procedure still further by starting with a single state, either 0, or 0_σ^+ for a particular value of σ; but to obtain motional phenomena complete expressions such as those given by (42) must be used.

Radiation and a Free Charged Particle. Photons

The results obtained above suggest the following general picture of the action of monochromatic radiation upon a free electron or other charged particle.

Beginning at one extreme, we may have the particle so closely controlled in momentum that the Compton recoil $h\nu/c$ is much greater than the spread or indefiniteness in momentum of the particle, the position of the latter being then indefinite to the extent of many wave-lengths of the radiation. The principal effect of the radiation in this case is to produce an internal statistical distribution of momentum and a resultant spreading of the packet, which, being proportional to the first power of the time, easily out distances the spreading required by the indetermination principle and so results in the phenomenon of the recoil electrons. This Compton spreading, being confined to the forward hemisphere relative to the incident rays, involves a forward acceleration of the packet centroid; we have thus, in physical terms, radiation pressure but no force corresponding to an electric or magnetic field of the type usually associated with electromagnetic waves. Theoretically such a case can be realized at any frequency whatever.

If we now progressively decrease the indefiniteness of position and at the same time unavoidably increase the indefiniteness of momentum, different quantum states in the packet eventually begin to combine in (25) and (27) and so by "interference" to cause the classical motion of the packet as a whole. At the same time the Compton recoil becomes progressively more and more masked by the initial indefiniteness in momentum of the particle and therefore harder to distinguish from the latter in observation. This change in the phenomenon reaches an advanced stage when the packet "diameter" becomes equal to the wave-length of the radiation.

Finally, when the whole packet becomes very much smaller than a cubic wave-length and at the same time sufficiently well-defined in momentum so that it will stay small during many field-periods, then we have the fully developed classical case. The Compton shift in momentum is now so small that it is altogether lost in the general initial blur of the momentum; the elementary radiation pressure represented by this shift must at the same time pass somehow into the classical radiation pressure. The smallness of packet requisite for this case can be secured initially for any wave-length of radiation, but this condition can be made to last during many periods only if the wave-length considerably exceeds the "Compton wave-length", $\lambda = h/mc$, or 0.0242A for electrons and less in proportion to the mass for heavier ions.

In the centroid motion, when thus fully developed, there is no trace of

the billiard-ball action which is characteristic of the Compton effect and which suggests so strongly the existence of photons. One might explain the absence of such discontinuities by pointing out that under those conditions in which the classical motion is actually observable there would always be very many photons acting, so that any discontinuities in the elementary processes would be smoothed out. In the usual photon formulation of radiation theory, however, the photons are associated with the quantum states themselves, a state s with quantum numbers $N_{\sigma s}$ being regarded as one in which there are $N_{\sigma s}$ photons moving in each of the directions $\boldsymbol{n}_\sigma$, whereas we have seen that the centroid motion arises as a combination effect between these states. It seems unlikely that a satisfactory law can ever be found which would represent the centroid velocity as arising in a simple way from many impulses imparted independently by the separate photons. The preferable view seems to be that the photon is, like a wave on the ocean, not an ultimate building block of the world but merely a special form or appearance that sometimes takes shape.

LOCAL MOMENTUM IN WAVE MECHANICS. II

By Lloyd A. Young*
Massachusetts Institute of Technology
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Abstract

It is shown that in the limit $h \to 0$ the quantity local momentum becomes equal to the classical momentum and the equations involving local momentum become equations of classical mechanics. Operators are found for this quantity corresponding to the operator $(h/2\pi i)(d/dx)$.

1.

THE most usual statement concerning the relation of quantum to classical mechanics is that in the limit $h \to 0$ quantum mechanical relations connecting the observables of this theory pass over into classical equations. One of the most important of such relations is the commutator of matrix mechanics

$$\boldsymbol{px} - \boldsymbol{xp} = \frac{h}{2\pi i}\boldsymbol{1}$$

connecting the dynamical variables $\boldsymbol{p}$ and $\boldsymbol{x}$. In the limit $h = 0$ we obtain the following results for $\boldsymbol{p}$ and $\boldsymbol{x}$: (1) they become commuting quantities of the classical theory (2) they are simultaneously observable to any degree of accuracy. The above results along with the behavior of the quantum mechanical equations of motion are sufficient to show that, if we represent the motion of a system by a wave packet, in the limit $h \to 0$ (1) the initial size of the packet may be made as small as we please, (2) the wave packet does not spread, and (3) it moves in accordance with the laws of classical mechanics. The above is not intended as a proof that

$$\lim_{h \to 0} (\text{quantum mechanics}) = \text{classical mechanics}$$

but is simply an outline of the steps which might be taken in such a proof.

In a recent issue of the Physical Review the author published a paper ("A Note on Local Momentum in Wave Mechanics")[1] in which it was shown that the wave functions for one-dimentional problems could be written in the forms

$$\begin{aligned} \psi^+ &= P(x)^{-1/2} e^{2\pi i/h \int P dx} \\ \psi^- &= P(x)^{-1/2} e^{-2\pi i/h \int P dx} \end{aligned} \tag{1}$$

or for discrete states[2]

$$\psi = P(x)^{-1/2} \cos \frac{2\pi}{h} \int P dx \tag{2}$$

* National Research Fellow.

[1] Young, Phys. Rev. **38**, 1612 (1931).

[2] For discrete states we require $(2\pi/h)\int P dx = n\pi$ the range of integration being taken over the entire range of the coordinate. Note that twice the integral makes the analogy with the Bohr-Sommerfeld quantum condition $\oint p dx = nh$ complete.

where $P(x)$ (called local momentum) satisfies the differential equation

$$P^2 + 2m(V - E) = \frac{h^2}{4\pi^2} P^{1/2} \frac{d^2}{dx^2} P^{-1/2}. \tag{3}$$

The Bohr-Sommerfeld quantum condition was there revived in terms of the local momentum and it was stated that in the limit, $P(x)$ becomes equal to $p(x)$, the classical momentum. This may be demonstrated easily from Eq. (3) for if we go to the limit $h = 0$ we obtain

$$P^2(x) + 2m(V - E) = 0 \tag{4}$$

but classically we have

$$p^2(x) + 2m(V - E) = 0$$

Therefore in the limit $h \to 0$, $P(x) \to p(x)$. If in Eq. (3) we introduce $S_h = \int P dx$ we obtain as $h \to 0$

$$\left(\frac{dS_0}{dx}\right)^2 + 2m(V - E) = 0. \tag{5}$$

This is the one-dimensional Hamilton-Jacobi equation, S_0 is the classical action function and S_h its wave mechanical analogue.

It is clear that $P(x)$ is not a dynamical variable but it is interesting to try to find an operator $\boldsymbol{P}$ corresponding to the operator $\boldsymbol{p} = (h/2\pi i)(d/dx)$. To do this let us consider a wave function of the form ψ^+. Let us answer the question as to what function $Q(x)$ satisfies the relation

$$\frac{h}{2\pi i} \frac{d}{dQ(x)} \psi^+ = P(x)\psi^+ \tag{6}$$

We find

$$\frac{dQ}{dx} = \frac{h}{2\pi i} P^{-1} \frac{d}{dx} \log \psi^+ \tag{7}$$

introduction for ψ^+ its value in terms of $P(x)$ and integrating yields

$$Q(x) = x + \frac{1}{4\pi i} \cdot \frac{h}{P(x)} \cdot \tag{8}$$

Note that for finite h the last term in this equation is just $1/4\pi i$ times a "de Broglie wave-length" and that in the limit $Q(x) \to x$ the dynamical variable conjugate to p. $Q(x)$ also satisfies

$$\frac{h}{2\pi i} \frac{d}{dQ} \psi^- = - P(x)\psi^- \tag{9}$$

Moreover we may write

$$\begin{aligned} \psi^+ &= e^{2\pi i/h \int P dQ} \\ \psi^- &= e^{-2\pi i/h \int P dQ} \end{aligned} \tag{10}$$

and the real wave function

$$\psi = \cos(2\pi/h) \int P dQ. \tag{11}$$

So far the author has discovered no real practical advantage in writing the wave functions in this form but their simplicity has a definite elegrance and aesthetic value. If we define an operator $\boldsymbol{P}$ by the relation

$$\boldsymbol{P} = \frac{h}{2\pi i}\frac{d}{dQ}$$

we can easily show that

$$\boldsymbol{P} = \left[1 + \frac{1}{4\pi i}\frac{d}{dx}\left(\frac{h}{P(x)}\right)\right]\boldsymbol{p}. \tag{12}$$

It is clear from our definition of the operator $\boldsymbol{P}$ that

$$\boldsymbol{PQ} - \boldsymbol{QP} = \frac{h}{2\pi i}\boldsymbol{1}$$

but a more significant relation may be derived, namely

$$\boldsymbol{PQ} - \boldsymbol{QP} \equiv \boldsymbol{px} - \boldsymbol{xp}. \tag{13}$$

These results are interesting and suggestive and may be extended easily. We consider that a close and fundamental relationship has been established between the local momentum $P(x)$ and the classical momentum.

2.

The differential equation satisfied by $P(x)$, Eq. (3), is not in a form which allows easy analytic calculation, but, by making use of the relationship existing between $P(x)$ and the fundamental solutions of the Schrödinger equation for the same potential, analytic expressions may be obtained for most of the well-known equations of wave mechanics whose solutions are known exactly. By taking $P^{-\frac{1}{2}}$ as the dependent variable Eq. (3) may be put into a form admirably suited to numerical methods. As might be expected results of problems depending essentially on wave interference may be expressed simply in terms of the phase integral $\int P dx$. For example, consider the elastic scattering of electrons by atoms represented by a central field of potential $V(r)$ (Ramsauer effect). We obtain the well-known result for the cross section in units equal to the square of the Bohr radius for hydrogen

$$Q = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l \tag{14}$$

where

$$\delta_l = \lim_{r\to\infty}\left[\int_0^r P_{1,l}(r)dr - \int_0^r P_{0,l}(r)dr\right] \tag{15}$$

where the $P_{1,l}$ and $P_{0,l}$ are the local momenta corresponding to the wave equations

$$R''_{1,l} + \left[k^2 + 2V(r) - \frac{l(l+1)}{r^2}\right]R_{1,l} = 0 \tag{16}$$

and

$$R''_{0,l} + \left[k^2 - \frac{l(l+1)}{r^2}\right]R_{0,l} = 0 \tag{17}$$

In these equations k^2 represents the energy of the electron beam in hydrogenic units.

THE FIRST SPARK SPECTRUM OF CAESIUM (Cs II)

By O. Laporte, G. R. Miller, R. A. Sawyer
University of Michigan

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Abstract

The resonance lines of Cs II have been photographed in the ultraviolet region with the vacuum spectrograph. The mode of excitation was the hollow cathode discharge in helium. The values of the wave-lengths of the ultraviolet lines for Cs II were obtained from second order measurements. With the separations of the resonance lines as guides, it was possible to assign electron configurations to the energy levels given by Sommer and to extend his scheme somewhat. The coupling is that of approximate (*jj*) type. The characteristic feature of the Cs II spectrum was the decomposition of the levels arising from the various configurations into two distinct groups due to the large separation of the $5p^5\ ^2P$ of Cs III. Five of the eight resonance lines found in the ultraviolet region fitted into Sommer's scheme. One new level with $J=0$ has been found in this investigation, thus completing the group of the six $5p^56p$ levels built upon the $^2P_{11/2}$ limit. The classification, assignment of inner quantum numbers, and the identification of levels agreed with the theoretical considerations as well as with the predictions from the Xe I classification. The remaining three resonance lines appeared to be due to transitions from the $5p^6\ ^1S_0$ ground level to new $5p^5(s, d)$ levels built upon the $^2P_{1/2}$ limit. It was possible to separate the $^3P_2$ and $^3P_1$ levels due to $5p^5$ ($^3P_{1\,1/2}$) (6*s* and 7*s*) from the $5p^5(^2P_{1\,1/2})$ (5*d* and 6*d*) levels. The ionization potential of Cs II was computed to be approximately 23.4 volts.

I. Introduction

IN A recent publication the authors have presented a classification of the Rb II spectrum[1] which was made possible by the identification of the resonance lines of the spectrum in spectrograms taken with a vacuum spectrograph of a hollow cathode discharge of rubidium in helium.[2] The present paper gives the result of a similar undertaking for caesium. The procedure was the same as for rubidium. The caesium metal was placed in a molybdenum hollow cathode and the spectrum excited by a discharge in an atmosphere of helium. It was photographed with a 1 meter vacuum spectrograph and the wave-lengths of the resonance lines determined by measurements in the second order against carbon and helium standards. As reported in a preliminary communication,[3] eight lines were measured between 962A and 612A. These data were made use of to interpret the material of Sommer,[4] who photographed the caesium spark spectrum in the region λ3268–7280 and arranged a number of the lines in a scheme showing recurring frequency differences.

[1] O. Laporte, G. R. Miller, R. A. Sawyer, Phys. Rev. **38,** 843 (1931).

[2] Through a remarkable oversight the potassium arc resonance lines, λλ7664 and 7698, were classified in the Rb II spectrum. These two lines and the term by which they were classified should be striken out of that paper.

[3] O. Laporte, G. R. Miller, R. A. Sawyer, Phys. Rev. **37,** 845 (1931).

[4] Sommer, Ann. d. Physik **75,** 163 (1924).

The Cs II spectrum is, like that of Rb II, of rare gas type. The lowest term is $5p^6\ {}^1S_0$ and the higher terms with which we are concerned arise from the excitation of one of the p-electrons to an s, p, d, or f level of higher quantum number. A tabulation of the number and location of the levels to be expected from each of these configurations on both the Russell-Saunders and the (jj) coupling is given in Table I which is repeated here for convenience

TABLE I. *Electron configurations and theoretical terms of the Cs II spectrum.*

Electron configuration	Russell-Saunders						(jj)		Number of levels
$4p^5$	^2P						$^2P_{1\frac{1}{2}}$	$^2P_{1\frac{1}{2}}$	
$4p^6$	$^1S_0$						0		(1)
$4p^5 5s$ $4p^5 6s$ $4p^5 7s$ —	$^1P_1$				$^3P_{210}$		12	01	(4)
$4p^5 5p$ $4p^5 6p$ $4p^5 7p$ —	$^1S_0$	$^1P_1$	$^1D_2$	$^3S_1$	$^3P_{210}$	$^3D_{321}$	12 0123	01 12	(10)
$4p^5 4d$ $4p^5 5d$ $4p^5 6d$ —	$^1P_1$	$^1D_2$	$^1F_3$	$^3P_{210}$	$^3D_{321}$	$^3F_{432}$	0123 1234	12 23	(12)
$4p^5 4f$ $4p^5 5f$ $4p^5 6f$ —	$^1D_2$	$^1F_3$	$^1G_4$	$^3D_{321}$	$^3F_{432}$	$^3G_{543}$	1234 2345	23 34	(12)

from the rubidium paper. However, whereas in the Rb II spectrum the coupling was of a type intermediate between the Russell-Saunders and (jj) cases, it is to be expected that in Cs II, as found in Xe I[5], the coupling will be nearly of the (jj) type and that the two groups of terms having as limits $^2P_{1/2}$ and $^2P_{1\ 1/2}$ of the Cs III spectrum will be completely separated. This indeed is found to be the case and in fact all of the levels found by Sommer are built upon the $5p^5\ ^2P_{1\ 1/2}$ term of Cs III.

The scheme given by Sommer consists of transitions between a middle set of terms and a higher and a lower set. Our knowledge of the similar Rb II and Xe I spectra would identify the middle set of terms as belonging to $5p^5\ 6p$ and the upper and lower sets respectively to a blend of $5p^5\ 5d$ and $6s$ and of $5p^5\ 6d$ and $7s$ respectively. The ultraviolet lines must be transitions between the lowest term in the spectrum, $5p^6\ {}^1S_0$ and the terms of the configurations $5p^5\ (6s, 7s, 5d, 6d)$ having $j=1$. Five of the ultraviolet lines in fact may be fitted into Sommer's scheme on this assumption. Table II gives the classified lines of Cs II and relative term values based on $^1S_0=0$. The first and second columns contain the spectroscopic notations[6] of the levels arising from the $5p^5\ 5d$, $5p^5\ 6d$, and $5p^5 6s$, $5p^5 7s$ configurations respectively, while the third column contains the J values of these levels. The fourth column con-

[5] Meggers, de Bruin and Humphreys, B. S. Jour. Research **3**, 731 (1929).

TABLE II. *Classification of lines of Cs II.*

$5p^5(^2P_{1\frac{1}{2}})5d$, $6s$				$5p^6$	$5p^5(^2P_{1\frac{1}{2}})6p$					
				$^1S_0$	1_1	2_2	3_3	4_1	5_2	6_0
d	s	J	→	0	1	2	3	1	2	0
		↓	Rel. Term Value ↓	→						
	$^3P_2°$	2	107392.28		19126.12 (8) −.14	20697.48 (6) −.07	21715.33 (10) −.04	22597.42 (2) 0	23373.78 (9) .06	
	$^3P_1°$	1	107904.93	107905. (20)	18613.42 (6) −.19	20184.84 (6) −.06		22084.85 (7) .16	22861.10 (6) .03	25248.63 (5) .02
$1_1°$		1	110945.14	110946 (20)	15573.14 (2) −.26	17144.51 (6) −.18		19044.61 (6) .03	19820.81 (6) −.05	22208.49 (7) .09
$2_2°$		2	112795.15			15294.63 (3) −.05	16312.38 (4) −.12	17194.57 (3) 0	17970.87 (7) .02	
$3_3°$		3	113716.65			14373.12 (4) −.06	15390.96 (3) −.04		17049.36 (1) .01	
$5p^5(^2P_{\frac{1}{2}})5d$, $6s$										
	$1_1°$	1	122872	122872 (20)						
	$2_1°$	1	123645	123645 (20)						
$5p^5(^2P_{1\frac{1}{2}})6d$, $7s$				$^1S_0$	1_1	2_2	3_3	4_1	5_2	6_0
d	s	J	→		1	2	3	1	2	0
		↓	Rel. Term Value ↓	→						
	$^3P_2°$	2	149212.24		22693.82 (7) .12	21122.47 (4) .06	20104.64 (5) .05		18446.14 (5) −.14	
	$^3P_1°$	1	149605.32	149604. (12) −1.32	23086.95 (4) .17	21515.53 (5) .04		19615.46 (4) −.14	18839.20 (3) −.12	16451.65 (2) −.13
$1_1°$		1	152172.11	152172. (5) −.11	25653.67 (7) .10	24082.27 (4) −.01		22182.32 (2) .07	21406.02 (4) −.09	
$2_2°$		2	152791.47		26273.12 (6) .17	24701.59 (4) −.05	23683.75 (3) −.07	22801.61 (5) −.14	22025.41 (6) −.06	
$3_2°$		2	153302.26		26783.83 (2) −.06	25212.38 (6) −.05	24194.54 (2) −.07	23312.46 (7) −.08	22536.21 (0) −.05	
$4_3°$			153556.59			25466.74 (6) −.02			22790.50 (0) .09	
$5_3°$		3	153678.19			25588.30 (4) −.06	24570.52 (6) −.02		22912.15 (9) .10	
$6_1°$		1	156399.34	156392. (12) −7.34		28309.51 (0) 0		26409.65 (5) .03	25633.22 (0) −.12	23245.86 (6) .06
$5p^5(^2P_{\frac{1}{2}})6d$, $7s$										
	$1_1°$	1	163180	163180 (7)						

tains the relative term values of the levels of these configurations and are referred to the $5p^6\ {}^1S_0$ level. The headings of the remaining columns give the spectroscopic notations[6] and relative term values (referred to $5p^6\ {}^1S_0$) of the levels due to the $5p^6$ and $5p^5(^2P_{1\frac{1}{2}})\ 6p$ configurations. In the body of the table are the wave numbers of the spectral lines, followed in parenthesis by their intensities. Below each wave number is the discrepancy (observed value minus calculated value) between the observed wave number and the wave number calculated from the positions assigned to the levels. The scheme is essentially that of Sommer with the addition of terms of relative value 122872, 123645, 133153 and 163180 and the lines arising from them.

Table III contains a list of Cs II lines classified in this investigation. In the first two columns are the intensities obtained in the two investigations; in the third column are the λ's and the wave numbers in vacuum; the last column contains the classification. $(5p^5)$ is omitted in the classification since it

TABLE III. *Wave-length list of Cs II lines.*

Int.		λ air I.A.	ν vac.	Classification
M	*S*			
7		612.82 (vac.)	163180	$5p^6\ {}^1S_0-(^2P_{1\frac{1}{2}}6d,\ 7s)1_1^\circ$
12		639.42 "	156392	$5p^6\ {}^1S_0-(^2P_{1\frac{1}{2}}6d)6_1^\circ$
5		657.15 "	152172	$5p^6\ {}^1S_0-(^2P_{1\frac{1}{2}}6d)1_1^\circ$
12		668.43 "	149604	$5p^6\ {}^1S_0-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
20		808.77 "	123645	$5p^6\ {}^1S_0-(^2P_{\frac{1}{2}}5d,\ 6s)2_1^\circ$
20		813.85 "	122872	$5p^6\ {}^1S_0-(^2P_{\frac{1}{2}}5d,\ 6s)1_1^\circ$
20		901.34 "	110946	$5p^6\ {}^1S_0-(^2P_{1\frac{1}{2}}5d)1_1^\circ$
20		926.75 "	107905	$5p^6\ {}^1S_0-(^2P_{\frac{1}{2}}6s)^3P_1^\circ$
	0	3531.376	28309.51	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}6d)6_1^\circ$
	2	3732.539	26783.83	$(^2P_{1\frac{1}{2}}6p)1_1-(^2P_{1\frac{1}{2}}6d)3_2^\circ$
	5	3785.424	26409.65	$(^2P_{1\frac{1}{2}}6p)4_1-(^2P_{1\frac{1}{2}}6d)6_1^\circ$
	0	3804.66	26276.13	
	6	3805.096	26273.12	$(^2P_{1\frac{1}{2}}6p)1_1-(^2P_{1\frac{1}{2}}6d)2_2^\circ$
	0	3805.42	26270.85	
	0	3896.52	25656.65	
	7	3896.978	25653.67	$(^2P_{1\frac{1}{2}}6p)1_1-(^2P_{1\frac{1}{2}}6d)1_1^\circ$
	0	3897.340	25651.31	
	0	3900.09	25633.22	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)6_1^\circ$
	4	3906.933	25588.30	$(^2P_{1\frac{1}{2}}5p)2_2-(^2P_{1\frac{1}{2}}6d)5_3^\circ$
	0	3925.12	25469.74	
	6	3925.583	25466.74	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}6d)4_3^\circ$
	0	3925.94	25464.41	
	5	3959.495	25248.63	$(^2P_{1\frac{1}{2}}6s)^3P_1^\circ-(^2P_{1\frac{1}{2}}6p)6_0$
	0	3959.870	25246.25	
	6	3965.187	25212.38	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}6d)3_2^\circ$
	0	3965.54	25210.13	
	4	4047.184	24701.59	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}6d)2_2^\circ$
	6	4068.773	24570.52	$(^2P_{1\frac{1}{2}}6p)3_3-(^2P_{1\frac{1}{2}}6d)5_3^\circ$
	0	4069.19	24568.21	
	2	4132.003	24194.54	$(^2P_{1\frac{1}{2}}6p)3_2-(^2P_{1\frac{1}{2}}6d)3_2^\circ$
	4	4151.267	24082.27	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}6d)1_1^\circ$
	0	4220.571	23686.83	
	3	4221.119	23683.75	$(^2P_{1\frac{1}{2}}6p)3_2-(^2P_{1\frac{1}{2}}6d)2_2^\circ$
	0	4276.56	23376.73	$(^2P_{1\frac{1}{2}}6s)^3P_2^\circ-(^2P_{1\frac{1}{2}}6p)5_2$
	9	4277.100	23373.78	

[6] Since it is impossible to assign L and S values to the levels, the levels were numbered according to their order, and the inner quantum number was given as lower index to this number. The odd configurations are indicated with a small zero as upper index.

TABLE III. (*Continued*).

Int.		λ air I.A.	ν vac.	Classification
M	*S*			
	0	4287.80	23315.43	
	7	4288.350	23312.46	$(^2P_{1\frac{1}{2}}6p)4_1-(^2P_{1\frac{1}{2}}6d)3_2^\circ$
	1	4288.755	23310.26	
	6	4300.636	23245.86	$(^2P_{1\frac{1}{2}}6p)6_0-(^2P_{1\frac{1}{2}}6d)6_1^\circ$
	4	4330.239	23086.95	$(^2P_{1\frac{1}{2}}6p)1_1-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
	0	4362.70	22915.17	
	9	4363.275	22912.15	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)5_3^\circ$
	0	4363.69	22909.97	
	6	4373.018	22861.10	$(^2P_{1\frac{1}{2}}6s)^3P_1^\circ-(^2P_{1\frac{1}{2}}6p)5_2$
	0	4373.43	22858.91	
	5	4384.428	22801.61	$(^2P_{1\frac{1}{2}}6p)4_1-(^2P_{1\frac{1}{2}}6d)2_2^\circ$
	0	4386.566	22790.50	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)4_3^\circ$
	7	4405.253	22693.82	$(^2P_{1\frac{1}{2}}6p)1_1-(^2P_{1\frac{1}{2}}7s)^3P_0^\circ$
	0	4405.69	22691.56	
	2	4424.046	22597.42	$(^2P_{1\frac{1}{2}}6s)^3P_2^\circ-(^2P_{1\frac{1}{2}}6p)4_1$
	0	4436.06	22536.21	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)3_2^\circ$
	7	4501.525	22208.49	
	0	4501.98	22206.24	$(^2P_{1\frac{1}{2}}5d)1_1^\circ-(^2P_{1\frac{1}{2}}6p)6_0$
	0	4502.56	22203.36	
	2	4506.834	22182.32	$(^2P_{1\frac{1}{2}}6p)4_1-(^2P_{1\frac{1}{2}}6d)1_1^\circ$
	0	4526.12	22087.79	
	7	4526.725	22084.85	$(^2P_{1\frac{1}{2}}6s)^3P_1^\circ-(^2P_{1\frac{1}{2}}6p)4_1$
	0	4527.19	22082.55	
	6	4538.942	22025.41	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)2_2^\circ$
	0	4539.40	22023.17	
	0	4603.11	21718.37	
	10	4603.755	21715.33	$(^2P_{1\frac{1}{2}}6s)^3P_2^\circ-(^2P_{1\frac{1}{2}}6p)3_3$
	0	4604.24	21713.04	
	5	4646.508	21515.53	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
	4	4670.280	21406.02	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}6d)1_1^\circ$
	4	4732.975	21122.47	$(^2P_{1\frac{1}{2}}6p)2_2-(^2P_{1\frac{1}{2}}7s)^3P_2^\circ$
	6	4830.161	20697.48	$(^2P_{1\frac{1}{2}}6s)^3P_2^\circ-(^2P_{1\frac{1}{2}}6p)2_2$
	6	4952.835	20184.84	$(^2P_{1\frac{1}{2}}6s)^3P_1^\circ-(^2P_{1\frac{1}{2}}6p)2_2$
	5	4972.593	20104.64	$(^2P_{1\frac{1}{2}}6p)3_3-(^2P_{1\frac{1}{2}}7s)^3P_2^\circ$
	6	5043.800	19820.81	$(^2P_{1\frac{1}{2}}5d)1_1^\circ-(^2P_{1\frac{1}{2}}6p)5_2$
	4	5096.604	19615.46	$(^2P_{1\frac{1}{2}}6p)4_1-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
	8	5227.002	19126.12	$(^2P_{1\frac{1}{2}}6s)^3P_2^\circ-(^2P_{1\frac{1}{2}}6p)1_1$
	6	5249.373	19044.61	$(^2P_{1\frac{1}{2}}5d)1_1^\circ-(^2P_{1\frac{1}{2}}6p)4_1$
	3	5306.609	18839.20	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
	6	5370.979	18613.42	$(^2P_{1\frac{1}{2}}6s)^3P_1^\circ-(^2P_{1\frac{1}{2}}6p)1_1$
	5	5419.687	18446.14	$(^2P_{1\frac{1}{2}}6p)5_2-(^2P_{1\frac{1}{2}}7s)^3P_2^\circ$
	7	5563.019	17970.87	$(^2P_{1\frac{1}{2}}5d)2_2^\circ-(^2P_{1\frac{1}{2}}6p)5_2$
	0	5563.73	17968.59	
	3	5814.181	17194.57	$(^2P_{1\frac{1}{2}}5d)2_2^\circ-(^2P_{1\frac{1}{2}}6p)4_1$
	5	5831.159	17144.51	$(^2P_{1\frac{1}{2}}5d)1_1^\circ-(^2P_{1\frac{1}{2}}6p)2_2$
	1	5863.701	17049.36	$(^2P_{1\frac{1}{2}}5d)3_3^\circ-(^2P_{1\frac{1}{2}}6p)5_2$
	2	6076.738	16451.65	$(^2P_{1\frac{1}{2}}6p)6_0-(^2P_{1\frac{1}{2}}7s)^3P_1^\circ$
	4	6128.619	16312.38	$(^2P_{1\frac{1}{2}}5d)2_2^\circ-(^2P_{1\frac{1}{2}}6p)3_3$
	2	6419.541	15573.14	$(^2P_{1\frac{1}{2}}5d)1_1^\circ-(^2P_{1\frac{1}{2}}6p)1_1$
	3	6495.528	14390.96	$(^2P_{1\frac{1}{2}}5d)3_3^\circ-(^2P_{1\frac{1}{2}}6p)3_3$
	3	6536.440	15294.63	$(^2P_{1\frac{1}{2}}5d)2_2^\circ-(^2P_{1\frac{1}{2}}6p)2_2$
	4	6955.519	14373.12	$(^2P_{1\frac{1}{2}}5d)3_3^\circ-(^2P_{1\frac{1}{2}}6p)2_2$

is common to all configurations lying above the $5p^6\ ^1S_0$ ground state. The odd configurations are indicated by an upper index.

II. Indentification of Levels and Configurations in Cs II

At first inspection, the energy level diagram presented in Table II and schematically in Fig. 1 exhibits a marked difference from the corresponding

diagram for rubidium.[7] The most characteristic dissimilarity is the smaller number of levels which were found by Sommer, e.g., while in all rare-gas-like spectra, the number of the middle group of p terms is ten, Sommer found only five, to which this present investigation added a sixth level. The explanation of this difference is that due to the large separation of $5p^5\ ^2P$ term, which is the limit of these p terms, the ten p levels are split into two groups of 6+4,

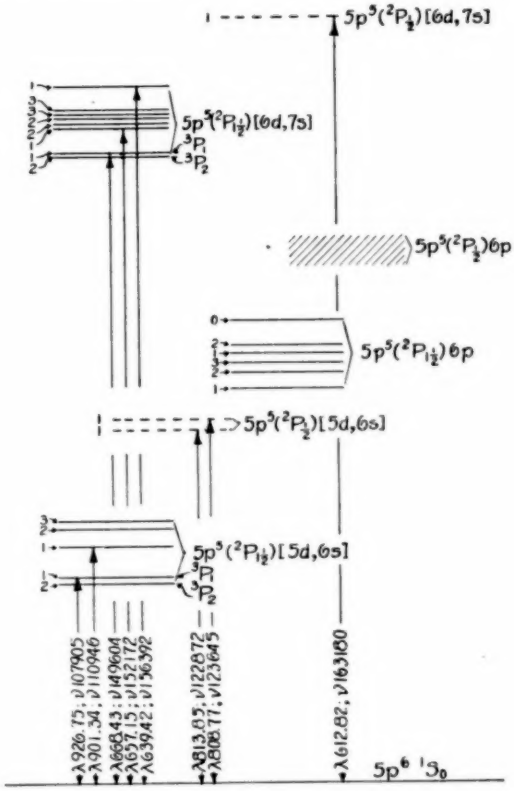

Fig. 1. Energy diagram for Cs II.

the inner quantum numbers of which are found under heading (jj) coupling in Table I. Comparing this table with the energy diagram for Cs I, it is seen that the six $5p^56p$ levels which are built upon the lower series limit $^2P_{1\ 1/2}$ are now all located. Likewise, only that part of the other configurations has been found which is built upon $^2P_{1\ 1/2}$; this is indicated in our notation by including the symbol $^2P_{1\ 1/2}$ in the spectroscopic notation.

From this point of view, the explanation of the additional resonance lines $\nu = 122872$, $\nu = 123645$, and $\nu = 163180$ is obvious (Fig. 1): they have as initial levels, those of the $5p^5(5d, 6s)$ etc., configurations which are built upon $^2P_{1/2}$. In Fig. 1 all levels which belong to the limit $^2P_{1/2}$ are drawn as dashed lines and are shifted slightly to the right.

[7] See Fig. 2 in reference 1.

[8] See Fig. 3 under reference 1.

The group of six middle levels must be assigned to $5p^5(^2P_{1\ 1/2})6p$. In the following diagram, (Fig. 2) we compare the separation of these levels with the corresponding group in Xe I, reducing, however, the Cs II separations by multiplication with 9120/14270, the ratio of the relativistic doublets in the two cases. There is no crossing over of the levels as in the case of Kr. I, Rb II[8]. In the limit of very high ionization, the six levels will form a group of two having the inner quantum numbers 12 and 0123.

The lower group of levels must be then those due to adding a $5d$ and a $6s$ electron. $6s$ can contribute only two levels. They will have $j=2$ and 1 respectively, lie close together and the one with $j=2$ will be the deeper. As there is no other alternative, we choose the lowest two levels, namely ν107392.28, ν107904.93 as $^3P_2$ and $^3P_1$.

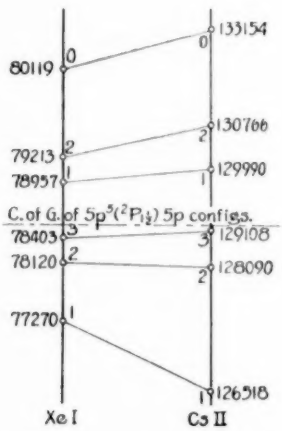

Fig. 2. The $5p^5(^2P_{1\,1/2})6p$ configurations of Xe I and Cs II referred to the center of gravity and reduced to the same magnitude of the relativistic doublet $5p^5$.

As far as the identification of the $5p^5(^2P_{1\ 1/2})5d$ levels is concerned, the result is rather incomplete. As Fig. 1 shows, only three more levels with $J=1$, 2, 3 are definitely established, while the J values 0,1,1,2,2,3,3,4, are expected. It seems however that the present experimental data are too scant to locate additional levels. It will be remembered that in the present spectrum, only Sommer's data for the visible are available, while in Rb II, Reinheimmer's wave-lengths were supplemented by Otsuka's measurements in the near ultraviolet.[1]

As a glance at the energy diagram (Fig. 1) shows, there is but little ambiguity in identifying the two lowest levels of the upper group ν14912.24, ν149605.31 as $5p^5(^2P_{1\ 1/2})7s\ ^3P_2$ and $^3P_1$. The fact that they lie well separated from the rest of the levels of that group speaks in favour of this assignment.

The result for the $5p^5(^2P_{1\ 1/2})6d$ levels is much more complete than for the previous series member. We have two levels each with inner quantum numbers 1, 2, 3, which is indeed what should be expected. Only one level with $J=0$ and another with $J=4$ remain to be discovered. It should be remembered however that as the latter one gives only one combination, with the $J=3$

level of $5p^56p$ there is no way to establish its existence conclusively, until additional configurations with which it might combine are known.

TABLE IV. *Classification of levels built upon* $5p^5\ ^2P_{\frac{1}{2}}$.

$5p^6\ ^1S_0-5p^5(^2P_{\frac{1}{2}})5d, 6s$	$5p^5\ (^2P_{\frac{3}{2}})5d, 6s-5p^5(^2P_{\frac{3}{2}})6p$				
122872 (20)	18689.34 (3)	1838.72	20528.06 (6)	1129.12	21657.19 (3)
773	770.05		770.18		770.32
123645 (20)	17919.29 (0)	1838.61	19757.88 (3)	1129.09	20886.87 (3)
$5p^6\ ^1S_0-5p^5(^2P_{\frac{1}{2}})6d, 7s$	$5p^5(^2P_{\frac{1}{2}})6p-5p^5(^2P_{\frac{1}{2}})6d, 7s$				
163180 (7)	21624.51 (4)	1838.60	19785.91 (3)	1129.26	18656.65 (0)

It will be remembered that in the spectrum of Rb II[1], the separation of the p^5s from the p^5d levels was essentially helped by the consideration of the hyperfine structure. The hypothesis was used that levels due to an s electron show wider hyperfine separations than those due to p or d electrons. In caesium however, a similar consideration failed to give any help; because not only is it to be expected that due to the much higher atomic number of caesium even the p electrons will split up into hyperfine structure levels, but also do the experimentally recorded hyperfine structure patterns occur in such an apparently haphazard fashion, that it proved to be impossible to correlate them in any way to the levels. The hyperfine structure data in Cs II seem much less complete than those in Rb II.

From Table II the separations between the first and second series numbers of $^3P_2$ and $^3P_1$ are found to be equal to 41820 cm^{-1} and 41700 cm^{-1} respectively. With the aid of the Rydberg term tables for spark spectra,[9] these differences were each fitted into a Rydberg sequence thus giving two independent determinations of the absolute term values:—

$$5s(^2P_{1\frac{1}{2}})^3P_2 - 6s(^2P_{1\frac{1}{2}})^3P_2 = 41820; \quad 5s(^2P_{1\frac{1}{2}})^3P_1 - 6s(^2P_{1\frac{1}{2}})^3P_1 = 41700$$

$$^3P_2 = 81685 \qquad ^3P_1 = 81505$$

$$5s(^2P_{1\frac{1}{2}})^3P_2 - {}^3P_1 = 512$$

$$^3P_2 = 82017$$

The agreement is fair. If we take the average value of $^3P_2 = 81851$, and subtract from it the $\Delta P(^3P_2-{}^3P_1=512)$, we obtain the $^3P_1$ absolute value as 81339 cm^{-1}. By adding the frequency of the resonance line λ926.75, ν107905 ($^1S_0-{}^3P_1$) to the $^3P_1$ term value we obtain.

$$^1S_0 = 189244 \text{ cm}^{-1}$$

as the calculated term of the normal caesium ion which corresponds to an ionizing potential of 23.4 volts. Mohler gives 21.5 ± 0.5 volts. It is however to be expected the limit determined from only the first s- terms will be somewhat low. The estimate is tentatively included as it seems to be well-founded.

[9] F. Paschen, J.O.S.A. and R.S.I. **16,** 231 (1928).

It was pointed out above that the additional resonance lines $\nu 122872$, $\nu 123645$ ($\Delta\nu = 773$) have as initial levels, those of the $5p^5(5d, 6s)$, while $\nu 163180$ has that of $5p^5(6d, 7s)$; all three combinations are built upon $^2P_{1/2}$. Sommer's data have been gone over thoroughly for the difference 773, but so far except for a few differences given in Table IV, we have been unable to find a satisfactory system of levels. An attempt is now being made in this laboratory to extend the experimental data on the spark spectrum of caesium and it is hoped that it will be possible to locate the terms built on the $^2P_{1/2}$ limit.

At this time the authors wish to express their appreciation to Mr. John F. Wagner who assisted in making the photographic exposures.

THE THEORY OF THE EXCITATION OF ATOMIC MERCURY BY ELECTRON IMPACT

By W. G. Penney*
University of Wisconsin

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Abstract

The probability of excitation by electron impact of the four P levels (2^1P_1, 2^3P_2, 2^3P_1, 2^3P_0) of Hg has been calculated. It is found that, although with increasing velocities the excitation of two of the triplet levels vanishes compared with that of the singlet, that of the middle triplet level approaches a small constant value (1/25), which can be calculated from the singlet-triplet separation. It is also possible to calculate the number of dispersion electrons f for these transitions by the use of approximate wave functions. Although the absolute magnitude of f is too large by a factor 2, the relative magnitudes are fixed by the singlet-triplet separation and are in good agreement with experiment. An estimate is made of the relative probability of excitation of all four P levels for fairly slow electrons, and these are roughly all of the same order of magnitude, the ratios at 10 volts being 7.0:3.5:1.9:0.4. The variation of the cross sections with voltage are shown in the figure. A brief comparison with experiment is given.

THE theoretical treatment of the problem of the excitation of atoms by electron impact is one which has recently attracted a great deal of interest. Considerable success has been obtained but there are so many different factors entering into the theory that it is difficult to take account of them all. Neglect of any one of these will tend to spoil agreement with experiment under any conditions where this particular feature is of importance. For example, when the velocity of the exciting electrons is high the effect of electron interchange can be neglected and the incident and scattered electrons can be considered as plane waves, but this is not the case for slow electrons. The importance of taking into account electron exchange has been shown by Oppenheimer[1] and Massey and Mohr,[2] the latter authors having worked out the scattering in atomic hydrogen and helium. They obtain very good agreement with the experimental results for the variation with velocity of the effective cross sectional areas corresponding to transitions of the atom to various excited states. Faxen and Holtsmark,[3] Holtsmark[4] and Allis and Morse[5] have considered the scattering of slow electrons by collision with atomic systems, without however, taking into account electron interchange. They find a large variation of the cross section with the velocity, in agreement with experiment.

* Commonwealth Fellow.

[1] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[2] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. **A132**, 605 (1931).

[3] H. Faxen and J. Holtsmark, Zeits. f. Physik **45**, 307 (1927).

[4] J. Holtsmark, Zeits. f. Physik **48**, 231 (1928); **52**, 485 (1929); **55**, 437 (1929); **66**, 49 (1930).

[5] W. P. Allis and P. M. Morse, Zeits. f. Physik **70**, 567 (1931).

As is well known, the spectrum of a two-electron system, such as helium or mercury, consists of singlets and triplets. If the spectrum is excited optically, then on account of selection rules, the singlet levels do not combine with all of the triplets. If the method of electron impact is used to excite the atom, there results immediately the possibility of exciting the atom into any one of the triplet levels as well as into the singlets. This arises on account of the rearrangement of the electron spins, accomplished by an interchange between an atomic and the incident electrons. The interesting thing to be calculated is the relative excitation probability of the four P levels (viz., 2^1P_1, 2^3P_2, 2^3P_1, 2^3P_0.) of mercury, this being chosen because it is easy to work with experimentally. The following investigation attempts to extend the calculations of Massey and Mohr in two directions. Firstly, according to their calculations, the probability of excitation of the triplet levels becomes vanishingly small as the electron velocity is increased. Actually we shall show that for inter-system lines it approaches a fairly small asymptotic value because the wave functions appropriate to these levels are not entirely antisymmetric in the orbital part alone. Secondly, we shall make an estimate of the relative probabilities of excitation of all three components of the triplet and compare them with that of the singlet. In order to preserve uniformity of notation we shall follow Massey and Mohr as closely as possible.

According to Dirac[6] the first order cross section for excitation of an atom from state n to state m, is given by

$$A_{nm} = 8\pi^3 m^2 k'/h^4 k' \sum_{m_s m_{s'}} | (n, \mathbf{k}, m_s | V | m, \mathbf{k}', m_s') |^2. \tag{1}$$

Here $\mathbf{k}h/2\pi m$ and $\mathbf{k}'h/2\pi m$ are the electron velocities before and after impact and V is the interaction energy. m_s and m_s' represent the spin of the incident and scattered electron quantised along some axis, for convenience the same as in the m_L, m_S representation for the atom. The effective cross section for all angles of scattering is then

$$A = \int_0^\pi A_{nm} \sin \delta d\delta$$

where δ is the angle of scattering.

In order to obtain the correct form for the wave functions of the complete system we must take combinations of atomic wave functions and plane waves, representing the incident and scattered electrons. We write

$$\Phi(1, 2, 3) = e^{ik\mathbf{n}_0 \cdot \mathbf{r}_3} \psi(1, 2)^{S_{\alpha_3}}_{S_{\beta_3}} + e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1} \psi(2, 3)^{S_{\alpha_1}}_{S_{\beta_1}} + e^{ik\mathbf{n}_0 \cdot \mathbf{r}_2} \psi(3, 1)^{S_{\alpha_2}}_{S_{\beta_2}} \tag{2}$$

It is now necessary to consider the wave functions of the mercury atom.

Wave Functions of the Hg Atom

The problem of the choice of suitable wave functions for the S and P levels of the mercury atom is one to which only an approximate answer can

[6] P. A. M. Dirac, Quantum Mechanics p. 179.

be given. We adopt the method of Slater,[7] writing the radial wave function for any electron in the form

$$R(r) = Nr^{n^*-1}e^{-Zr/n^*}[1 + A_1/rZ + A_2/r^2Z^2 + \cdots],$$

where $[Z/n^*]^2$ is the ionization potential for this electron in terms of Rh, and $A_n = -(n^*/2n)[(n^*-n)(n^*-n+1) - l(l+1)]A_{n-1}$. The radius r is measured in terms of a_0, the radius of the first Bohr orbit in hydrogen. In our problem we retain terms up to A_1. We adopt the value $Z=1.65$ for the s electrons in the ground state, 0.35 being Slater's estimate as to how much the electrons shield each other, and $Z=2$, $Z=1$ for the s and p electrons respectively in the excited P states. For the ionization potentials we take 10.4, 18.9[8] and 5.3 volts respectively, the last being chosen to give about the correct position of the four P levels. On substituting these values and introducing the angle variables we find for the three types of wave function

$$\begin{aligned}
\psi(s, S) &= R_{00}(r)/(4\pi)^{1/2} = (1.51/(4\pi)^{1/2})r^{0.87}e^{-0.88r}(1 - 0.92/r),\\
\psi(s, P) &= R_{01}(r)/(4\pi)^{1/2} = (3.03/(4\pi)^{1/2})r^{.69}e^{-1.18r}(1 - 0.50/r),\\
\psi(p, P) &= R_{01}(r)P_1{}^m(\cos\theta)e^{im\phi}\\
&= (0.421(3/4\pi(1 + m)!)^{1/2}r^{0.60}e^{-0.62r}(1 + 0.83/r)P_1{}^m(\cos\theta)e^{im\phi}.
\end{aligned}$$

To satisfy the antisymmetrical condition for the complete wave functions (i.e., inclusive of spin) it is necessary to take combinations of these simple functions. Houston[9] has shown that the S level can be written

$$\psi_S(1, 2) = R_{00}(1)R_{00}(2)1/2^{1/2}(S_{\alpha_1}S_{\beta_2} - S_{\alpha_2}S_{\beta_1}), \tag{3A}$$

and the four P levels

$$\psi_{PjM} = \sum_{i=1}^{4} a_{ijM}\phi_{ijM} \tag{3B}$$

and he gives formulae for the coefficients a. Here M is the component of j along some slight external field, assumed to remove degeneracy, and

$$\begin{aligned}
\phi_{1M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_1{}^M(2)R_{11}(2)e^{iM\phi_2}\\
&\quad + P_0{}^0(2)R_{01}(2)P_1{}^M(1)R_{11}(1)e^{iM\phi_1}]2^{-1/2}(S_{\alpha_1}S_{\beta_2} - S_{\alpha_2}S_{\beta_1}),\\
\phi_{2M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_1{}^{M-1}(2)R_{11}(2)e^{i(M-1)\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_1{}^{M-1}(1)R_{11}(1)e^{i(M-1)\phi_1}]S_{\alpha_1}S_{\alpha_2},\\
\phi_{3M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_1{}^M(2)R_{11}(2)e^{iM\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_1{}^M(1)R_{11}(1)e^{iM\phi_1}]2^{-1/2}(S_{\alpha_1}S_{\beta_2} + S_{\alpha_1}S_{\beta_2}),\\
\phi_{4M}(1, 2) &= 2^{-1/2}[P_0{}^0(1)R_{01}(1)P_1{}^{M+1}(2)R_{11}(2)e^{i(M+1)\phi_2}\\
&\quad - P_0{}^0(2)R_{01}(2)P_1{}^{M+1}(1)R_{11}(1)e^{i(M+1)\phi_1}]S_{\beta_1}S_{\beta_2}.
\end{aligned}$$

[7] J. C. Slater, Phys. Rev. **32,** 349 (1928); **57,** 36 (1930).

[8] H. N. Russell, Astrophys. J. **70,** 11 (1929).

[9] W. V. Houston, Phys. Rev. **33,** 297 (1929). Alternative schemes may be given corresponding with those of E. Wigner, Gruppentheorie p. 208, J. H. Bartlett Jr. Phys. Rev. **34,** 1247 (1929); **38,** 1623 (1931); and N. M. Gray and N. A. Wills, Phys. Rev. **38,** 248 (1931). A little care is needed to be consistent in the definition of matrix elements and differential operators as they are different in the different schemes.

The coefficients a are given in Table I.

TABLE I.

$S=0$ ——— $S=1$ ———

M_J	a_1	a_2	a_3	a_4
1	0.979	0.15	0.15	0
0	0.979	−0.15	0	0.15
−1	0.979	0	0.15	0.15

2^1P_1

1	0.207	0.69	0.69	0
0	0.207	−0.69	0	0.69
−1	0.207	0	0.69	0.69

2^3P_1

$S=0$ ——— $S=1$ ———

M_J	a_1	a_2	a_3	a_4
2	0	1	0	0
1	0	−0.707	0.707	0
0	0	−0.41	0.82	−0.41
−1	0	0	0.707	−0.707
−2	0	0	0	1

2^3P_2

0	0	0.577	0.577	0.577

2^3P_0

Dispersion Electrons

In order to test how good an approximation the radial wave functions are, we have calculated the number of dispersion electrons f per atom[10] for the transitions $1^1S_0 - 2^1P_1$, $1^1S_0 - 2^3P_1$. In our notation

$$f = (2\nu/3R)\left[\int_0^\infty R_{00}(r_1)R_{01}(r_1)r_1^2 dr_1 \int_0^\infty R_{00}(r_2)R_{11}(r_2)r_2^3 dr_2\right]^2,$$

ν being the frequency of the radiation associated with these transitions. We find 2.0 and 0.066, while the experimental values are 0.96 and 0.0255.[11] The agreement is satisfactory but shows that the value for a_1 for the level 2^3P_1 is too high, it being 0.207 according to Houston's formula instead of 0.185 from the experimental data. Since the f values are too large by a factor 2 we can expect the cross sections calculated from the same wave functions to be too large by a similar factor and this is what is found. However, as we are interested mainly in relative magnitudes, this is not a serious matter.

Substituting the atomic wave functions (3A) and (3B) in the expression (2) we obtain the wave functions for the complete system. Putting these in (1) for the cross sectional area and summing over the spins, it is found [12]

[10] See for example R. Ladenburg, Zeits. f. Physik **4,** 451 (1921) and Y. Sugiura, Phil. Mag. **4,** 495 (1927).

[11] R. Ladenburg and G. Wolfsohn, Zeits. f. Physik **65,** 207 (1931).

[12] The physical interpretation of this formula is as follows. The first term represents an electron coming away from the impact with the same spin as that of the incident electron; the second and third terms represent a turning over of the spin, the effect of which is to add or subtract 1 from M. To obtain the formula it is necessary to write out a large number of terms. The reader will have no difficulty in obtaining the result quoted if he will write out in full the following steps.

$$(S, \boldsymbol{k}, S_\alpha' \mid V \mid P, \boldsymbol{k}', S_{\alpha 3}) = \int Vdv\left[\sum P_{12_3}\psi_s(1,2)e^{i\boldsymbol{k}n_0\cdot r_4}S_{\alpha_2}\right]\left[\sum P_{12_3}e^{i\boldsymbol{k}'n_1\cdot r_4}S_{\alpha_3}\sum_{i=1}^{4}a_{ij}M\phi_{ij}M\right]^*,$$

$$A_{SPM} = k'/k[\,|\,a_1(F_M - G_M) + a_3 g_M\,|^2 + |\,a_2 g_{M-1}\,|^2 + |\,a_4 g_{M+1}\,|^2],$$

where

$$F_M = 2\pi m(2\pi)^{1/2} e^2 a_0^2 h^{-2} \int \phi_{1M}^*(1, 2) V \psi_S(1, 2) e^{i(k n_0 - k' n_1)\cdot r_3} dv,$$

$$G_M = 2\pi m(2\pi)^{1/2} e^2 a_0^2 h^{-2} \int \phi_{1M}^*(2, 3) V \psi_S(1, 2) e^{i(k n_0 \cdot r_3 - k' n_1 \cdot r_1)} dv,$$

$$V = \left(\frac{2}{r_3} - \frac{1}{r_{13}} - \frac{1}{r_{23}}\right),$$

and g_M is the same as G_M except that ϕ_2 is substituted for ϕ_1 in the integrand. These ϕ are just the orbital wave functions, the spin functions being omitted. n_0 and n_1 are unit vectors along the direction of motion of the incident and scattered electrons. To find the effective cross sectional area of the atom we must integrate over all angles of scattering and sum over all values of M. Now, as shown by Massey and Mohr[2], the integrals g_M and G_M are much smaller for $M=0$ than for any other values of M and therefore we can write with sufficient approximation

$$A_{SPM} = (k^1/k)[\,|\,a_1(F_M - G_M) + a_3 g_M\,|^2 + |\,a_2 g_{M-1} + a_4 g_{M+1}\,|^2].$$

Relative Cross Sections for Fast and Slow Electrons

Several interesting features come immediately out of this formula. For the level 2^3P_1, a_1 is small and for 2^3P_2, 2^3P_0, a_1 is zero. Remembering that g_0 is the only g that counts, we find by using the table that the relative cross sections for these three levels for *slow* electrons are in the ratio 3:5:1 respectively. This conclusion is not quite exact since the excitation potentials are not quite the same for all three. This ratio should be roughly that of the maxima of the peaks for the three triplet levels and since g falls off rapidly with increasing velocities, measurements at any velocity will always weight a higher energy level over a lower. The excitation probability decreases rapidly with increasing velocities and for 30 volts g and G are very small. Hence for *fast* electrons it is only the F term which gives anything, so that, although the 2^1P_1 level still remains strong, the only other one left is 2^3P_1, with intensity about 1/25 that of the former, and this ratio should persist for all higher velocities. This latter conclusion can be clearly seen in the experimental results of Larché[13] on cadmiun and zinc. One would expect quite similar results in the case of mercury. If it were not for the cascade effects the experimental value for the number of dispersion electrons would fix the relative cross sections for fast electrons for 2^1P_1 to 2^3P_1 at 34:1.

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where $\sum P_{123}$ means sum over the permutations of electrons 123 as exhibited in Eq. (2). On account of the spin integration the only non-vanishing terms are those from ϕ_1 and ϕ_2 and the contribution of this matrix component to the cross section (1) is $(k'/2k)\,|a_1(F_M - G_M) + a_3 g_M\,|^2$. The component $(S_{\beta_3}; S_{\beta_3})$ gives a similar amount and $(S_{\alpha_3}; S_{\beta_3})$, $(S_{\beta_3}; S_{\alpha_3})$ the second and third terms respectively.

[13] K. Larché, Zeits. f. Physik **67**, 440 (1931).

Ratio of Singlet to Triplet for Intermediate Speeds

In order to obtain an idea of the relative magnitude of the singlet to triplets for slower electrons it is necessary to evaluate the various integrals. The integration over the angular coordinates is exactly the same as that explained by Massey and Mohr.[2] While it is possible to obtain F satisfactorily g and G are very complicated. In the first place the nodes in the wave functions are of importance. Moreover, it is necessary to consider at least the first two terms in the expansion of $1/r_{12}$ in associated Legendre polynomials. The simplest type of integral occuring is

$$\int_0^\infty \int_0^\infty r_1^a e^{-br_1}(1 + c/r_1)J_{3/2}(kr_1)\gamma_\nu(r_1, r_2)r_2^d e^{-fr_2}(1 + g/r_2)J_{1/2}(k'r_2)dr_1dr_2,$$

where $\gamma_\nu(r_1, r_2)$ is of the form $r_1^\nu/r_2^{\nu+1}$ or $r_2^\nu/r_1^{\nu+1}$ (ν integer), according as r_2 or r_1 is the greater. The only possible method of evaluating the integrals seemed to be to choose a velocity and then evaluate them numerically. When this is done there is still the integration over δ. Only rough accuracy therefore is claimed.

To obtain some idea of the physical meaning of the fact that although F decreases only slowly with velocity, G and g decrease rapidly, we may roughly describe the state of affairs as follows. F measures the chance that an electron, represented as a plane wave of a certain wave-length and extending from $+\infty$ to $-\infty$ through the atom, should change over into another plane wave of slightly different wave length, also extending from $+\infty$ to $-\infty$ but moving in a different direction. If the angle between the directions of motion of the two electrons is small the two waves are nearly the same, and there is quite a good chance that the influence of the atom will cause the transition. Directly the angle increases the waves differ appreciably and the chance of transition decreases rapidly. We see now why most of the scattered electrons are not deviated much from their original direction and this is particularly the case at high velocities. G and g represent quite a different effect; their interpretation is that an incident plane wave should be changed over into an atomic wave function and at the same time an atomic wave function be changed over into a scattered plane wave. This is easy when the wave-lengths of the electrons (i.e., the electron velocity small) are greater than the diameter of the atom but it becomes increasingly difficult as the electrons are speeded up, and directly there are two or three wave-lengths in atomic dimensions G and g drop nearly to zero.

Comparison with Experiment

The general behavior of the excitation probabilities is shown in Fig. 1. The agreement with the experimental values is good although there are no really satisfactory measurements available. I have to thank Professor J. T. Tate for the information that the relative probabilities of $2^3P_1 : 2^3P_2 : 2^1P_1$ are quite materially functions of the electron speed and at 10 volts are in the ratio 2.26:3.5:6.6 (the calculated values being about 1.9:3.5:7.0). The

probability of 2^3P_0 is very small indeed (we find 0.4). Moreover at this energy 2^1P_1 is increasing while the others are decreasing. These measurements apply only to those electrons which are not deviated much from their forward path by impact. Whitney[14] and Foard[15] have also made measurements on the energy losses in mercury vapor and their experimental results are in good agreement with our conclusions. Foard succeeded in resolving the 4.9 and 5.5 groups but only for primary voltages of about 6 volts. Referring to Fig. 1 it is seen that this is the most suitable region for resolution, the losses being not very different and quite large and the 6.7 loss not present at all. Whitney did not attempt to resolve the triplets but grouped them all together. His curves for the variation of cross section with voltage agree very well in character with ours but seem to attach more importance to the triplet levels at

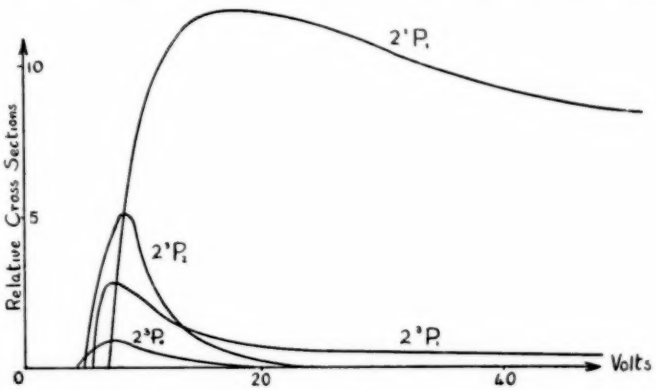

Fig. 1.

low voltages than we do. However the measurements are so difficult that there is no finality at present. Since we have considered only first order cross sections the agreement is extremely good. As far as the absolute magnitude of the cross section is concerned, it seems that the values obtained are too high. The experimental cross section for all types of collision is about $10\pi a_0^2$ at 200 volts and $6\pi a_0^2$ at 400 volts. For the 2^1P_1 level we get $3\pi a_0^2$ at 200 volts and $2\pi a_0^2$ at 400 volts, while it is even greater at smaller velocities. That excitation to one excited level, even though that be easily the most important, should account for $\frac{1}{3}$ or more of the total cross section seems too high an estimate. Apparently the error is due to the use of wave functions with insufficient nodes.

In later papers it is hoped to investigate the polarization of the hyperfine components excited by electron impact and also to extend these calculations to higher order cross sections.

I should like to express my thanks to Professor J. H. Van Vleck for many helpful suggestions during the course of this work.

[14] J. D. Whitney, Phys. Rev. **34**, 923 (1929).
[15] C. W. Foard, Phys. Rev. **35**, 1187 (1930).

SHOT EFFECT IN SPACE CHARGE LIMITED CURRENTS

By E. W. Thatcher and N. H. Williams
Union College and University of Michigan

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Abstract

The shot effect in space charge limited currents from tungsten and thoriated tungsten has been investigated. The effective fluctuation level is recognized, in general, as the combination of a depression due to pure space charge, and an elevation due to the liberation of electrons by positive ions. The magnitude of the elevation may be such as to carry the fluctuation level far above that for the same current under temperature limitation, or it may simply alter the form of the depression curve. The abnormal fluctuations observed have been analyzed, and their cause traced to inherent mixed emission from the metal surface. The effect of age and heat treatment has been studied for specimens of tungsten. A double grid tube has been used for obtaining a space stream consisting solely of electrons, and the conditions determined under which this stream is governed by the laws of pure chance applying in the simple shot effect theory. With this arrangement space charge measurements of fluctuations can be made over a considerable range with the same degree of precision attainable with temperature limited currents. Considerations involving statistical correlation between instantaneous values of the anode current provide a possible theoretical basis for the space charge depression of shot effect. This treatment yields an expression for the ratio of the mean square value of the fluctuation voltage under given space charge conditions to that under strict temperature limitation of the current:

$$\bar{V}_s^2/\bar{V}_t^2 = f(i_0/i)e^{-\omega^2/2\alpha^2}$$

i_0 is the space current, i, the saturation current, or total emission associated with a particular emitter temperature, and their ratio characterizes the space charge situation. It has been shown that in the absence of abnormal effects, the depression of the mean square fluctuation voltage which results is independent of the frequency, $\omega/2\pi$, at which it is measured. This conclusion provides information regarding the spread of the correlation function defined in the theoretical section. A relation showing the fluctuation depression proportional to the square of the current depression under space charge is indicated.

§1.

THE study of spontaneous current fluctuations which occur in a circuit containing a thermionic element has given rise to new problems of considerable interest concerning the nature of the emission, and the passage through space of the charged particles. Treated theoretically first by Schottky[1] and later by Furth,[2] Ornstein and Burger,[3] and Fry[4] these manifestations of the atomic nature of electricity have come to be grouped under the general designation of the "shot-effect".

[1] Schottky, Ann. d. Physik **56,** 541 (1918).
[2] Fürth, Phys. Zeits. **23,** 354 (1922).
[3] Ornstein and Burger, Ann. d. Physik **70,** 622 (1923).
[4] Fry, Jour. Frank. Inst. **199,** Feb. (1925).

A technique of experimental investigation first successfully carried out by Hull and Williams[5] involves the use of a frequency selective screen grid vacuum tube amplifier of four or five stages. The thermionic current is caused to flow through an external tuned circuit of high impedance, and the fluctuations in potential across this unit are impressed upon the grid of the first amplifier tube. With a modification of the formula derived by Schottky for the mean square value of the fluctuation in potential, adapted to the particular circuit in use, Hull and Williams succeeded in determining the charge of the electron within a probable error of less than 1 percent.

Extension of this work and improvement of the technique has been reported in several recent papers. Particular mention should be made of the introduction of the aperiodic shot circuit,[6] the measurement of the charge carried by the K+ thermion,[7] and the studies in abnormal shot effect which have been carried out during the past year.[8,9]

It has been the practice to refer to those effects as abnormal where the conditions underlying the theory are not fulfilled, and where, as a result, the value of the electronic charge computed in the customary way departs from the accepted value.

The results of Johnson[10] at low frequencies have been interpreted by him, and further analyzed by Schottky[11] on the basis of an independent effect due to secular changes in the emission characteristics of the cathode.

Following are enumerated in brief form the essential postulates which must be fulfilled by the thermionic discharge under the normal shot effect theory. Experiment should provide:

(1) Emission consisting entirely of similarly charged carriers (electrons or ions as the case may be).

(2) Complete evacuation of the space surrounding the emitter.

(3) Random distribution of emission over the surface of the emitter.

(4) Random distribution of emission in time. (The number of electrons escaping from any section of the emitter in a small element of time should be independent of the number escaping from other sections and during adjacent time intervals. Only under these conditions do the simple probability relations apply to the emission.)

(5) Full reproduction at the collector of the random distribution of the emission. This involves the absence of interaction between carriers during their passage, and is realized only when the thermionic current is strictly "temperature limited".

(6) Freedom from sources of fluctuation in the circuit other than those due to the discreteness of charge of the particles.

[5] Hull and Williams, Phys. Rev. **25,** 147 (1925).
[6] Williams and Vincent, Phys. Rev. **28,** 1250 (1926).
[7] Williams and Huxford, Phys. Rev. **33,** 773 (1929).
[8] Donal, Phys. Rev. **36,** 1, 172 (1930).
[9] Kozanowski and Williams, Phys. Rev. **36,** 1,314 (1930).
[10] J. B. Johnson, Phys. Rev. **26,** 71 (1925).
[11] W. Schottky, Phys. Rev. **28,** 74 (1926).

The complete realization of the situation outlined by these postulates is, of course, impossible. By the use of well-evacuated tubes, low current densities, and high fields, the assumptions may be met to a degree of approximation within the limits of the experimental error. This was accomplished in the original work on the electronic and ionic charge.

It was early observed that when either the current density was large or the potential difference small, the mean square voltage fluctuations $\overline{V^2}$ fell below the value indicated for the normal shot effect.

The presence of even a small amount of gas in the tube was found to be responsible for abnormal effects of enormous and rather uncertain magnitude. With some types of emitters, particularly those employing a coating of barium and strontium oxides, elevations rather than depressions of the value of $\overline{V^2}$, were also observed when space charge limitation obtained. This effect was traced to the liberation of electrons from space charge by positive ions. By the device of mounting an electron emitter and a positive ion emitter in the same tube, the source of these abnormal fluctuations was definitely established by Kozanowski and Williams.[12]

It has been the aim of this research to investigate the effects of electron space charge on the fluctuations in a circuit carrying a thermionic current from tungsten and thoriated tungsten emitters.

In part, the observed decrease in fluctuation level with increasing space charge density finds its explanation in the cutting off of a certain fraction of the electron stream. Electrons whose velocities of emission are insufficient to carry them against the reversed field to the potential minimum of the space charge region will eventually be returned to the cathode. These, of course contribute nothing either to the average value of the anode current or to the fluctuations in the external circuit.

However, it appeared that the reduction in fluctuation level was more rapid than the change in current ratio would warrant. A theory proposed by Uhlenbeck sought to explain this behavior on the basis of statistical correlation between instantaneous values of the anode current. One consequence of this hypothesis is the prediction of a change of the space charge depression as the frequency of the amplifying system is changed.

Experiments made during the summer of 1930 by the writers and Kozanowski seemed to provide some evidence of a trend with frequency. The range between 54,000 and 190,000 pps was covered in these tests. Commercial tubes having thoriated tungsten filaments of the inverted "V" type were used, the grid and plate being connected together so as to form a two-element tube. From the inconsistencies and wide variations in results however, it became evident at the start that it would be necessary to find ways of analyzing these variations, and elimination of the errors which they introduce. Discrepancies as wide as five to ten percent were observed under experimental conditions which were reproducible certainly within two percent.

Commerical tubes with tungsten filaments were next investigated, and

[12] Kozanowski and Williams, Phys. Rev. **36,** 1314 (1930).

irregularities of the same general character observed. It appeared that the net depression might be the resultant of opposing influences, at least one of which was not consistent from one test to another. From previous work it was thought that the tendency to elevation of the fluctuation level might be traceable to the action of positive ions in electron space charge. Since the effects persisted at potentials below the lowest possible ionizing potentials, and since they were observed in notably "hard" commercial tubes, an impure emission was suspected as the underlying cause. A program of experiments was then undertaken with three main objects in view:

(1) To demonstrate the presence of positive ions in the emission and to show that the observed irregularity was produced by their action on the field in space charge.

(2) To devise a means of obtaining pure electronic emission governed by the laws of probability.

(3) If the second object could be realized, to study the effect of pure electron space charge on the normal shot effect with especial reference, as indicated in the theory, to the frequency dependence of the depression ratio and its connection with the total emission or saturation current.

§2

Apparatus and Experimental Procedure

It is necessary here to make brief reference to the experimental arrangement used in this work and the type of measurements undertaken. A five stage, screen-grid amplifier with tuned impedance coupling formed the essential unit. The amplifier with all auxiliary circuits is mounted in a double mesh screened cage within which the experimenter works. An oscillator for calibration and impedance measurement is located in a separate smaller cage several meters distant.

The amplifier response is detected by a 1000 ohm thermojunction coupled with a few turns of wire to the coil in the plate circuit of the last stage. The associated galvanometer reading is proportional to the square of the junction current, and therefore to the square of the output voltage. For a standard input, the current from the oscillator is passed through an inductance potentiometer of accurately concentric cylinders. The potential drop may be computed from the length used, and provides high frequency voltages of the required order of magnitude. The current in this circuit is read by a Western Electric type 20-D vacuum thermocouple and galvanometer. Strict proportionality between this reading for various currents and that of the output galvanometer indicates a linear characteristic for the amplifier. If this is maintained and checked at intervals, the absence of appreciable regeneration is assured.

When measurements involve absolute determinations, as of the electronic charge, the amplifier must be calibrated and the area under its resonance curve accurately determined. It is of course essential that this factor remain unchanged during the course of a series of readings.

The fluctuation circuit is enclosed in a copper box shield. The plate potential is supplied by a bank of dry cells in convenient 45 volt blocks with continuous variation provided by a potentiometer arrangement. The space current, indicated by a Weston four range microammeter, is passed through a wire resistor, R of about 30,000 ohms. The emitter is heated by a storage battery of 2–12 volts. The cathode, the high potential side of the anode circuit, and the shield are all maintained at ground potential for high frequency currents by the use of suitably located by-pass condensers, each of 1 mf capacitance.

The observed magnitude connected with the fluctuations is the deflection of the output galvanometer, G_0. This is a measure of the mean square output voltage, $\overline{E^2}$, and $\overline{E^2}$ is directly proportional to the mean square input voltage, $\overline{V^2}$. It was shown by Williams and Vincent that for the aperiodic shot circuit

$$\overline{E}^2 = 2A_0^2 A\epsilon i_0 Z^2 \tag{1}$$

where A_0 is the voltage amplification at the resonant frequency, A is the area under the relative response curve of the amplifier, ϵ the electronic charge, i_0 the mean emission current, and Z the parallel impedance of the input circuit, measured at the natural frequency of the amplifier.

If the fluctuation current be expressed in a Fourier series, we find for the mean square value of the kth component of the input voltage,

$$\overline{V}_k^2 = \tfrac{1}{2}C_k^2 Z_k^2 = 2zZ_k^2 \epsilon i_0 \frac{\omega_k}{2\pi k}$$

(see appendix, note 1, Eq. (9))

Since in Eq. (1), the factors A and A_0 are constant

$$\overline{V}_k^2 \sim \epsilon i_0 \sim \frac{\overline{E}^2}{Z^2} \sim \frac{G_0}{Z^2}.$$

The "depression ratio" is then given by

$$\frac{(\overline{V}_k^2)_s}{(\overline{V}_k^2)_t} = \frac{(G_0)_s}{(G_0)_t}\left[\frac{Z_t}{Z_s}\right]^2, \tag{2}$$

where the subscript s refers to a particular space charge limited current, and t to the temperature limited current at the same temperature of the emitter.

In practice the deflections of the galvanometer are not constant, but show a continual variation covering usually less than 5 percent of the scale. Readings may be determined either by watching the path of the scale in the telescope for perhaps 30 seconds and making a mental average, or by arithmetically averaging a large number of independent readings taken at random. The former method has a considerable advantage in the amount of time required, and was used in most of the work. The difference between the values of the deflection arrived at by the two methods is insignificant. The estimated maximum error for either is about 1 percent.

The impedance of the shot circuit is measured in essentially the following way. Current from the oscillator tuned to the peak frequency of the amplifier is passed through a standard variable condenser, and measured by means of a W. E. vacuum thermocouple. The drop across this unit is impressed upon the shot circuit, and the impedance calculated from the resulting current. The thermocouples used in these measurements are calibrated on the alternating current bridge described by Williams and Huxford.[13]

For temperature limited currents the maximum error estimated for this last determination is $\frac{1}{2}$ of 1 percent. In space charge measurements there seems no reason to question the validity of the method unless the impressed alternating electromotive force used in the impedance measurement becomes comparable to the potential difference between the electrodes of the tubes.

§3.

Abnormal Fluctuations in Space Charge Limited Currents

The fulfillment of the requirements mentioned in the first section for the study of fluctuations in space charge limited currents has been accomplished only through the introduction of additional means of control of that current. It was at first thought that the solution to the problem lay in simplification. In the preliminary work with commercial tubes of the 201-A type the grid and plate were connected together, forming essentially a two-element tube. The shape of these elements was recognized as unfavorable and the resulting effect on the field uncertain. It was expected however that any particular space charge condition, whatever its nature, could be reproduced by the suitable re-setting of the filament current, space current and plate potential.

As a matter of interest, and for the sake of continuity, mention is made here of the first attempts in the direction of simplification. A two-electrode tube was constructed with concentric cylindrical elements of the following dimensions:

		Diameter	Length
Filament	Tungsten	0.1 mm	24 mm
Plate	Nickel	16 mm	29 mm

The tube was sealed onto an evacuating system and the pressure reduced to 10^{-5} mm of mercury. The unit was then baked with an electric furnace for two hours at about 350°C. The metal parts were outgassed by heating to a bright red heat with a high frequency induction furnace. During the process the filament was heated continuously, and in the final stage of the treatment a current twenty percent greater than any planned for subsequent operation was used. Two magnesium "getters" were mounted at right angles to each other so that one could be flashed after the outgassing had been completed, while the tube was still on the pump, and the other after it had been sealed off. The abnormal effects observed—namely, elevation of the fluctuation level in space charge rather than the depression indicated by the theory—were attributed

[13] Williams and Huxford, Phys. Rev. **33,** 773 (1929).

at first to the evaporation of the sputtered film of magnesium on the filament, which resulted from flashing the getters.

The obvious means of avoiding this difficulty was to eliminate the use of a getter entirely. When this was done the desired pressures could be maintained only by continuous operation of a mercury pump. Tubes of identical construction with the one described above were sealed to a pumping system which was connected by a large tube to an outlet within the shield box of the shot circuit. A coil type liquid air trap prevented the diffusion of mercury vapor from the pump or the McLeod gauge used to indicate the pressure. Outgassing and baking were carried out as before and pressure readings less than 10^{-6} mm of mercury were maintained during the periods of observation.

It became apparent at once that even with the possibility of gaseous ionization and evaporation of sputtered films eliminated, abnormal space charge effects remained. The character of the abnormality was such as to indicate strongly an emission of mixed nature, and further study was made in verification and enlargement of this view. Similar effects have been observed by Kozanowski in the emission from oxide-coated cathodes, and here the disturbance was definitely traced to the simultaneous emission of positive ions and electrons. The influence of an ion upon the field in its vicinity is connected with its mobility. A simple calculation based on the kinetic theory yields the result that this effect for a positive ion of mass M is on the order of 140 $(M)^{1/2}$ times the effect of an electron. As a consequence, it can be shown that fluctuations of many times the normal level are to be expected as a result of the release from space charge by a single ion, of many electrons.

In reports by L. P. Smith[14] and H. B. Wahlin[15] the emission of positive ions by hot metals has been presented. Mass-spectrograph measurements with tungsten and molybdenum show that as the temperature is raised, first, ions of atomic mass corresponding to the alkaline earth metals are given off. Later, ions of greater atomic mass, and finally, ions of the metal itself, are evolved. It is difficult to explain the appearance of ions other than those of the metal specimen under observation unless those substances are present as impurities. Wahlin reports the persistence of the specific ion in a large group of metals while the emission of other ions is of a more transient character.

The tungsten obtained for the emitters in the present work was specified as chemically pure by the manufacturers. This apparently indicates only that precautions are taken during its manufacture to avoid contamination. Wire from two different sources was tried with no marked difference apparent in behavior.

A set of curves showing the effect of age and heat treatment of the tube is given in Fig. 1. A constant space current of 500 microamperes was maintained by raising the filament temperature as the plate voltage was reduced. Above thirty volts the curves are all seen to converge toward the common level for temperature limited currents. In the early stages of the tube history

[14] Smith, Phys. Rev., **33,** 381 (1930).
[15] Wahlin, Phys. Rev. **37,** 467 (A) and 473 (A) (1931).

no depression below this level is indicated. This simply means that the elevation due to release of electrons by positive ions is greater than the depression which might occur in the absence of such disturbing influence.

During the interval indicated between *C* and *D* the filament was operated at 1.2 amperes with a *negative* potential of 200 volts applied to the plate. After this treatment an actual depression was observed for the first time. It will be noted however that as the filament current was increased (to maintain constant space current) the trend of the curve turns upward. This is also apparent in the later curves. In general as the temperature approached that at

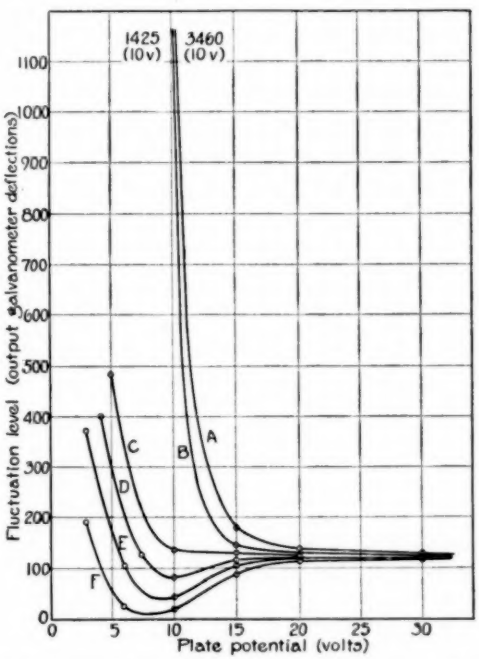


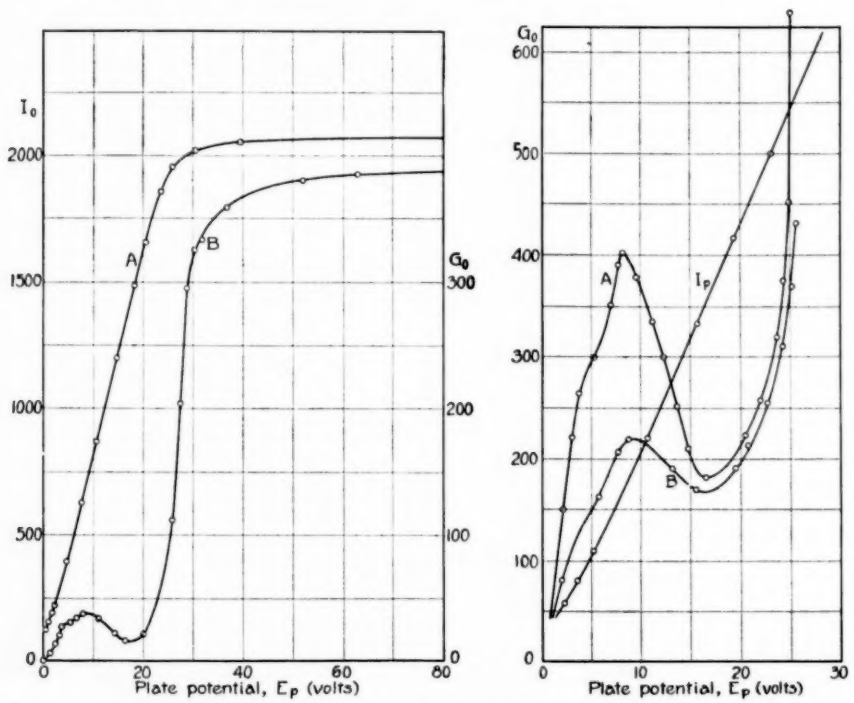
Fig. 1. Fluctuations in space charge limited currents from tungsten. Space current maintained constant by raising filament temperature. Curves $A-F$ represent successive stages in aging and heat treatment of specimen. All approach normal shot effect level when current becomes temperature limited. *A*—First heating of filament. *B*—After first outgassing. *C*—After repeated outgassing, pressure 10^{-6} mm—20 hrs. *D*—Filament aged 30 minutes, $E_p = 200v$, $I_f = 1.2$ amp. *E*—Filament aged 3 hours. *F*—Filament aged 9 hours.

which the aging process was carried on the depression gave way to an elevation. Curve *F* represents somewhat of a limiting situation, and subsequent data clustered around the level indicated at this stage after nine hours aging.

From the form of the curves of Fig. 1, it was recognized that changes in the emission characteristics of the filament were in large measure responsible for the elevation of the fluctuation level observed at low voltages. It should be pointed out that the excessive positive ion emission indicated in these tests results from the abnormally high temperatures necessary to maintain constant current under heavy space charge limitation. Indeed, it is probable that in this range, appreciable currents can be secured largely by virtue of

neutralization of space charge by positive ions. Emission of this character, while of interest in connection with the present work would rarely be met in the normal operation of tungsten emitters. The possibility was considered that high temperatures alone might bring about changes in the emitting surface which could be the sole cause of the large fluctuations.

As a test of this question the transition between temperature limitation and space charge was carried out another way—with constant emitter temperature. The space current in this case varies with the applied voltage as shown in curve *A*, Fig. 2. On this account alone the fluctuation level as shown by the



Figs. 2 and 3. Abnormal fluctuations observed in space charge region when filament temperature is held constant. The persistence of a peak is evidence of mixed emission at normal operating temperatures. Curves *A* and *B*, Fig. 3, correspond roughly to curves *C* and *D*, Fig. 1.

output galvanometer would be expected to decrease proportionately as E_P is decreased. Previous experience under space charge conditions indicated a still more rapid decrease of $\overline{V^2}$. Interest in this case centers on the peak which appeared to break the regular fall of the G_0 curve when plotted against E_P. Since no change was made in the filament temperature we are forced to the conclusion that this is due to some cause inherent in the emission. In Fig. 3 two curves are shown which correspond in a rough way to curves *C* and *D* in the "constant current" group. A definite decrease in the height of the peak is coordinated with a period of aging the filament with a large negative potential on the plate. It is significant that the *position* of the maximum is not changed by this treatment and is therefore a *function only* of the space charge situa-

tion in the tube and not of the emission characteristics.* The magnitude of the peak on the other hand is associated, as was expected, with the rate of emission of positive ions. From this, correlated with evidence presented in the preceding sections, we feel that the *only contribution* of an increase in emitter temperature is the increase in specific emission, *both of electrons and positive ions*.

Emission from thoriated tungsten

For comparison with the results on tungsten, curves obtained with emission from thoriated tungsten are reproduced here. Fig. 4 is drawn to show the fall in the fluctuation level for a constant space current as E is decreased from a value providing temperature limitation. The two curves represent actual data taken on the same tube at different times. The difference in the shape of the elbow is characteristic of emission from thoriated tungsten.

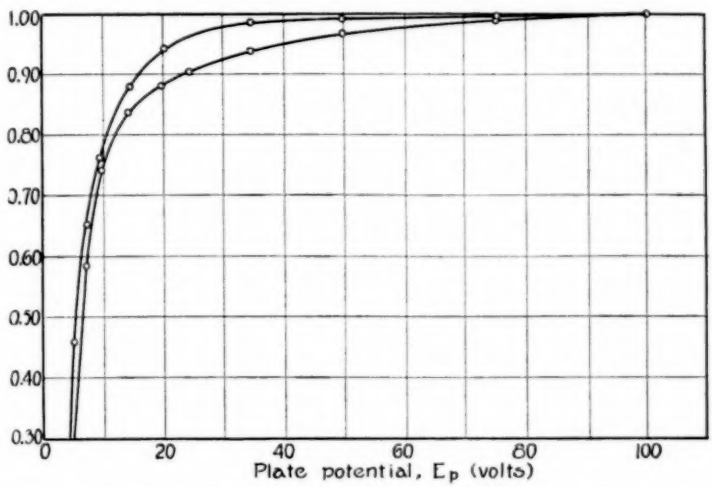


Fig. 4. Shot effect in emission from thoriated tungsten. Ordinates represent fractions of the normal fluctuation level. The spread between the two curves, taken under identical conditions is attributed to variation in the emission of positive ions. Constant space current $i_0 = 500 \mu$a.

There seems little doubt that the elevation of the fluctuation level due to positive ions in space charge is responsible for this irregularity in form. The abnormal fluctuation is simply superposed on the level resulting from the normal depression. The number of ions released at the temperature covered in these experiments is apparently insufficient to cause a resultant elevation. Further, the quantity varies with the time and previous treatment of the filament. This results in the region of uncertainty mentioned in connection with the preliminary work. It appears from the curves that this is greatest for a space current of 500 microamperes in the region of 20 volts on the plate. Below this, the curves seem to show greater uniformity. It must be borne in

* The filament current was actually held constant during runs of this type. The change in resistance due to the cooling effect of evaporation of electrons was less than one part in one thousand.

mind, however, that, due to the steepness of the slope and the low plate potentials used, experimental accuracy is considerably reduced.

Grid control of space charge

The effect of a space charge grid on fluctuations was next investigated. Tubes of cylindrical symmetry were built, with tungsten emitters, and provided, at first with grids 3 mm in diameter, and about 3 mm spacing between turns. Plates were of nickel, 16 mm in diameter.

Let us suppose, in line with the indication of previous results, that the emission consists mainly of electrons with a small quantity of positive ions. If we further assume that both types of emission occur with a chaotic distribution in time, we should expect, when potentials are adjusted to obtain continuous fluctuations. This was accomplished by applying a positive potential of 10–15 volts to the grid and 200 volts to the plate.

The establishment of space charge at any point in the tube resulted in a departure from this value. As an analysis of the fields in the tube will show, this may be due to an internal or external space charge referred to the grid. It is the latter, in which we are primarily interested, but it is essential to know the effect of internal space charge and the interaction with positive ions on the fluctuation levels. The use of a large positive potential on the grid would certainly result in the elimination of the inner space charge. The field would also be a retarding one for positive ions and would eventually cause the return of many of them to the cathode. Electrons, however, would suffer acceleration in the same field and their average velocity of appearance in the outer space would be much greater than the range of the original emssion velocities.

It is convenient to consider the region of the grid as a virtual emitter and to visualize the external space charge as produced by "emission" from the grid. It is at once apparent that for a given potential difference and current a larger emission velocity will result in a decreased space charge density. This follows from the relation $i = \rho v$ where i is held constant.

An experimental difficulty is encountered here in the extremely low voltages between grid and plate necessary to produce appreciable space charge density. This is concerned mainly with the accuracy of the measurements—in particular, the impedance determination, and is discussed in another section.

On the other hand, a *low* grid potential introduces space charge conditions in the inner space provided its field acts independently of that due to the plate potential. It was found necessary to cut the grid turn separation to about 0.4 mm to accomplish this shielding.

Since the *grid* and *filament* are connected together with only the small *fixed* potential difference between them, fluctuations between these two are logically assumed to be negligible. Both are held at earth potential for high frequency currents. We have to deal then only with grid or filament, whichever we choose. On this view the filament serves only as a source of electrons —the effective emission coming from the region of the grid.

It might appear that the existence of space charge in the inner space would not be of any significance in a measurement of these fluctuations. The design of a tube in which the external field was effectively screened from this space made possible a test of this question.

With the plate potential at 200 volts so that temperature limited conditions existed between plate and grid, the grid potential was carried in small steps over the range in which inner space charge was established. The variation of the $\overline{V^2}$ with E_g is shown in Fig. 5. The explanation of the eight-fold

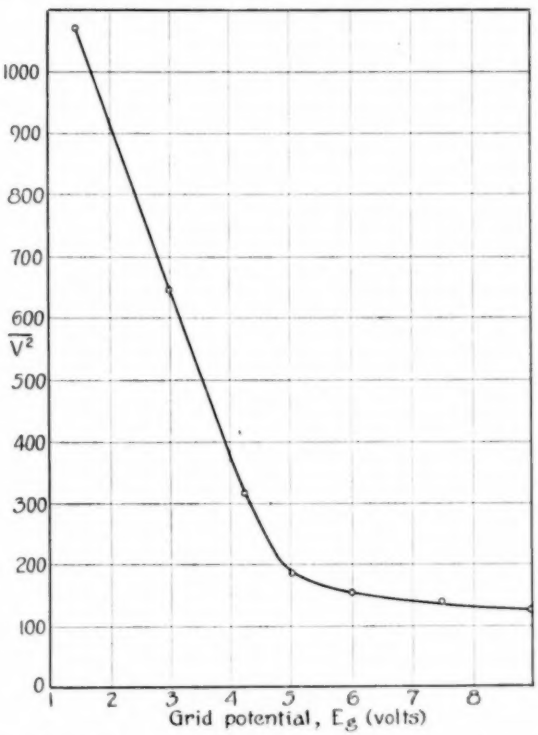


Fig. 5. Influence of positive ions in inner space charge in three element tube. Fluctuation level shown as a function of grid voltage, measured with respect to the negative terminal of the filament. The bend occurs at a value of E_g about equal to the filament drop in potential. E_p = 200 volts.

increase observed between $E_g = 6$ volts and $E_g = 1.5$ volts lies in the release of groups of electrons from the inner space charge by positive ions emitted from the filament. Moving toward the grid, some of these electrons are collected and some pass through into the grid-plate space. The "emission" from the virtual cathode therefore departs from a purely random character and the effect is observed in an elevation of the fluctuation level.*

The conclusion seems inevitable that when space charge conditions exist at *any* stage in the passage of a thermionic current, the action of positive ions will produce abnormal fluctuation effects.

* Grid and plate potentials in Fig. 5 are given with respect to the negative terminal of the filament. The bend in the fluctuation curve occurs when the value of the grid potential becomes equal to the drop along the filament due to the heating current.

In view of the extreme difficulty experienced in obtaining *pure* electron emission of reasonable intensity, this amounts to a requirement for the study of pure space charge effects that *the space charge must not occur in the immediate neighborhood of the emitter.*

§4

Pure Space Charge Effects

Field conditions in the double grid tube

These steps led to the introduction of a second grid, g_2 of Fig. 6, the function of which was two-fold:

1. To provide a retarding field for electrons after their passage through the inner grid space.

2. To shield the internal sections of the tube from the action of the external field.

The inner grid was held at a sufficiently high potential F_1 to assure the continuously positive field indicated in region A, Fig. 6. This serves the double purpose, first, of preventing the escape of positive ions into the sur-

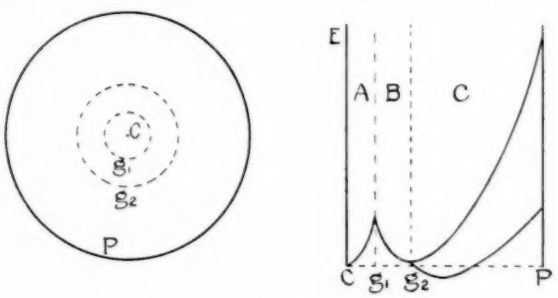


Fig. 6.

rounding space, and second, of maintaining within the region a temperature limited current whose fluctuations have been shown to be unaffected by positive ions. Electrons of zero initial velocity would arrive at g_1 with a velocity of E_1 volts. Some of course strike the grid and contribute to a measurable current which we shall call I_1. Others pass through the rather coarse mesh into the region B where a retarding field is maintained. The potential of g_2 is held only slightly positive with respect to the filament. As a result, the average emission velocity into region C is but slightly higher than the original emission velocity. Here again a portion of the electron stream is cut off constituting a current I_2.

Let us now examine the nature of the remaining emission. If g_2 be considered as a virtual emitter, we have a pure electronic space current in which space charge limitation may easily be set up by a suitable choice of the potentials E_p and E_2. It was anticipated that the accumulation of space charge in region B would cause a somewhat lower fluctuation level in this current than that obtained under temperature limitation in the simple two electrode

tube. Since the region in question, however, is free of positive ions, the only effect of this internal space charge will be an independent and constant depression. This is entirely different from the elevation produced by positive ions in an inner space charge which is of an irregular and uncontrollable magnitude.

Insofar, then, as our interest centers only on the influence of conditions in the outer space, an emission of the character described would appear to meet all the requirements. Gratifying results were immediately obtained in the increased accuracy of individual measurements. It became possible for the first time to repeat space charge measurements many times with an actual maximum spread in values of the depression ratio of about 2 percent.

The question as to whether the pure emission from the region of g_2 possesses the random character of true thermionic emission may be settled by measuring the mean square "shot" voltage with a high positive potential applied to the anode. A comparison of the values of $\overline{V^2}$ to those obtained with a two electrode tube under strict temperature limitation will immediately detect a departure from the ideal situation. For this comparison, tubes were chosen on which actual measurements of the electronic charge have been made. A value of $\overline{V^2}$ consistent with Eq. (1) and therefore a pure random emission fulfilling the postulates of the theory is assured. Tedious repetition of the complete calibration of the amplifier such as is necessary in the determination of ϵ were thus avoided since the same values of A_0 and A entered into each of the compared magnitudes.

Experiments were carried out to determine the optimum conditions for the production of space charge between the outer grid and the anode. A value of space current was chosen which produced sufficiently high electron density, and which could be maintained without danger to the filament. Grid potentials were then adjusted until the stream passing into region C exhibited fluctuations indentical with a temperature limited current from a metallic emitting surface.

The theoretical considerations outlined in the appendix Note A, lead to an expression for the fluctuation depression ratio:

$$\overline{V_s^2}/\overline{V_t^2} = f(i_0/i)e^{-\omega^2/2\alpha^2}$$

where $\overline{V_s^2}$ is the mean square voltage fluctuation under space charge conditions characterized by emission current i_0, space current i, and $\overline{V_t^2}$ the m.s. voltage fluctuation for a temperature limited current i. ω is 2π times the natural frequency of the amplifier curcuits, and α, a function defining the width of correlation.

Two questions are thus presented which invite investigation

(1) How great is the influence of the exponential term involving the frequency.

(2) In what manner does the depression of fluctuation level depend on the ratio of the collected current to the total emission current.

We will consider first the frequency effect.

The response characteristic of the amplifier has the form of a symmetric curve which falls off sharply on each side of the resonant frequency of the tuned circuits. The breadth of the curve can be controlled by the use of shunt resistors in these circuits. The area under the relative amplification curve is the factor A in the experimental Eq. (1). Thus from the wide range of frequencies represented in the Fourier analysis of the current fluctuations, only a narrow band is selected. Maximum amplification is afforded those components whose frequencies lie very close to the resonant frequency of the amplifier. By a choice of elements constituting the tuned impedance in the plate circuit of each stage, this band may be selected from various parts of the spectrum.

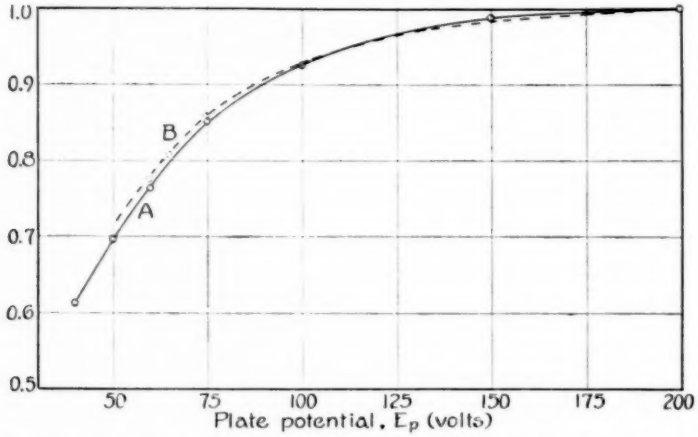


Fig. 7. Frequency dependence of space charge depression constant space current. Depression ratio as a function of E_p due to external space charge in double grid tube, E_1, E_2, and E_p measured from negative terminal of filament. A, 54,000 p.p.s. B, 480,000 p.p s. $i_0 = 500$ microamps. $E_1 = 9$ volts. $E_2 = 1.5$ volts.

The potential E_p actually applied to the anode of the "shot" tube is obtained from the impressed battery voltage by subtraction of the voltage drop across the series load. Starting with 200 volts or more E_p is decreased in steps, and the space current held constant by a corresponding increase in the filament temperature. Space charge is thus increased with decreasing E_p. The ratio of $\overline{V^2}$ for a certain current and applied potential to $\overline{V^2}$ for temperature limitation of the same current is obtained from the ratio of G_0/Z^2 for the two cases. (See Fig. 7.)

Each point on the curves is the average of at least twenty independent observations. These were part of a series of experiments on two different tubes which extended over a period of about ten weeks. Within two percent the average curves at 54,000 pps. and 480,000 pps. coincide throughout their length. We therefore feel justified in believing that the frequency effect on space charge depression is vanishingly small.

This conclusion furnishes an indication of the maximum breadth of the correlation function. If over a range covering nearly a ten fold increase in the

frequency, $e^{-\omega^2/2\alpha^2}$ does not depart appreciably from 1, $\omega^2/2\alpha^2$ must remain equal to zero. This can be true only if α is an extremely large quantity compared with ω. By reference to the role played by α in the correlation equation (Note A, Eqs. (4), (10))

$$\overline{j(t_1)j(t_2)} = \phi(t_1 - t_2) = \phi(w) = Pe^{-\alpha^2 w^2/2}.$$

We note that an extremely rapid decline of the function, ϕ is demanded. The width of the correlation band is thus shown to be *small compared to the shortest natural period of the amplifier.*

Since the frequency term reduces to unity, presumably $f(i_0/i)$ is a universal function representing the depression ratio of fluctuations in space charge. Let us follow the progress of a virtual emitting surface by considering its position in the tube to be that of the minimum potential between grid and anode. Under temperature limitations it coincides with g_2. As the space charge builds up the region expands and moves outward across the interelectrode space. A typical situation is represented by the lower potential curve in space *C*, Fig. 6. It is obvious that electrons will be retarded on entering this space and that those with initial velocities too low to reach the potential minimum will be returned in the direction of the cathode. Some of these returned charges strike the grid g_2. This number can be determined by the observed *change* in I_2. The field in the neighborhood of g_1 would lead one to expect a still greater change in I_1 and this is found when the collection current to this element is measured.

For any state, the total emission from g_2 is given closely by $I+\Delta I_1+\Delta I_2$ There is, of course, the possibility that a few electrons will reach the filament against the inner field. This number was thought to be negligible, and an independent check of the emission current by the application of a high potential to the plate showed this to be the case. Thus a reading of the emission current could be taken simultaneously with the determination of V^2.

The requirement of a large applied potential in comparison to those used in the impedance measurement prevents the determination of the mean square voltage fluctuation level with accuracy for low plate potentials. Restrictions imposed in turn by the maximum safe filament temperature, and the portions of the electron stream intercepted by the grids set an early limit upon increase of the emission current. When these are considered together it is found that the range of trustworthy and significant results is confined from two directions.

The emission from the region of minimum potential was measured by a direct current meter in the anode circuit, since all the electrons reaching this position are accelerated toward the collector. There seems to be no reason to believe that the probability relations governing the escape of electrons from the "cathode grid" will be changed in any way by the external field conditions in the tube. It was to be expected therefore that when the region lay near the grid, the current fluctuations would be identical with those of the stream passing through the grid. As space charge is increased in the outer space with

decreasing plate potential, the current reaching the anode falls off. The fluctuations, however, decrease more rapidly than the current. A comparison of these two effects is given in Fig. 8 in which f and its argument are both plotted against E_p.

The complete suppression of the shot effect fluctuations may be observed qualitatively by the behavior of the output galvanometer which falls to zero for very high space charge densities. The actual lower limit is fixed by the magnitude of the fluctuations due to the thermal agitation of electricity in

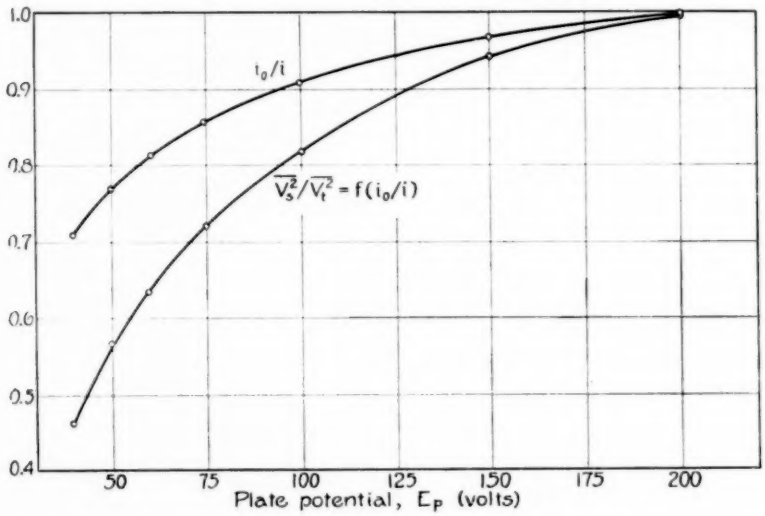


Fig. 8. Depression ratio of shot effect in space charge compared with ratio of anode current to emission current from the region of second grid. Between 50 and 200 volts. $i_0 = 500$ microamps. $E_1 = 22.4$ volts. $E_2 = 1.5$ volts.

the shot circuit. The mean square value of the voltage thus generated is of the order of 0.01 of the normal shot effect for a current of one milliampere. A correction can be made for this in the original galvanometer setting.

It may be of interest to record a rather striking empirical relation which may be obtained from the data presented in Fig. 8. Between $E_p = 50$ and 200 volts, it is true within experimental error that

$$\overline{V}_s^2/\overline{V}_t^2 = f(i_0/i) = (i_0/i)^2.$$

It is hoped that theoretical justification for this relation will be provided in the future.

ACKNOWLEDGMENT

It is a pleasure to acknowledge our indebtedness to Dr. G. E. Uhlenbeck for invaluable assistance during the investigation, and to Dr. A. W. Hull for helpful suggestions in the preparation of this report.

APPENDIX

Current Fluctuations

A simple thermionic device may consist of two electrodes sealed into a glass tube which is evacuated to such an extent that the residual gas plays no part in the discharge phenomena to be observed. One of the electrodes may be heated to any desired temperature below its melting point, and this is made the cathode in a circuit carrying the thermionic current.

Two fundamental sources of current fluctuation must be recognized in this circuit:

(1) The discreteness of the carriers of the current.

(2) The thermal agitation or "Brownian motion" of the electricity in the circuit.

In the case of a temperature limited thermionic current, the *first type* of fluctuation makes itself predominantly felt. Let us consider the flow of such a current in the simple circuit shown in Fig. 1. If the emission is a completely random effect, we may expect deviations from the long time mean value governed by the laws of probability. These fluctuations will be reproduced identically at the anode, with only the time of passage across the inter-electrode space intervening between the occurence of a particular event in emission, and its reproduction at the collector

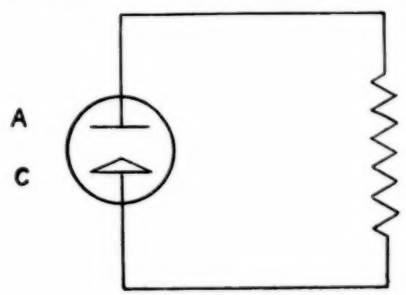


Fig. 1.

plate. As a result the potential of the plate will rise and fall chaotically about a certain mean value. The manifestation of the fluctuations in the electron stream, then, will be the development of small irregular alternating potential differences between separated points in the circuit.

It is clear in the normal shot effect that the fundamental fluctuating quantity is the number of electrons concerned in the emission from the cathode, and hence the *emission current*. The amplitudes of these particular fluctuations are of course independent of the frequency characteristics of the shot circuit or measuring device. The resulting potential fluctuations will involve the total impedance of the shot circuit which may be made practically free of frequency influence by the use of an aperiodic circuit.

Fluctuations of the *second type*—those due to the thermal agitation of electric charges—are always present in a conductor, whether carrying a current or not. Here the fundamental deviations from the long time mean situation are in the nature of *accidental electromotive* forces set up by random variations of charge density.

In section A we shall outline the theory of particle fluctuations in a thermionic current with particular emphasis on the effect of space charge. Following this a short discussion of thermal agitation is given, and the application to the present problem pointed out.

Note A. Amplitude of the Mean Square Deviation

Let $i(t)$ denote the instantaneous value of the thermionic current and $\bar{i}$ the long time mean value. The magnitude of the *deviation* from the mean may be developed in a Fourier series:

$$i(t) - \bar{i} = j(t) = \sum_{k=1}^{\infty} (A_k \cos \omega_k t + B_k \sin \omega_k t) \tag{1}$$

where

$$\omega_k = \frac{2\pi k}{\tau}$$

ω being the frequency in radians per second, and τ the fundamental period of the series. The coefficients of the kth term in the cosine and sine components of the general series are defined as follows:

$$\left.\begin{aligned} A_k &= \frac{2}{\tau}\int_0^\tau j(t)\cos\omega_k t\,dt = \frac{2}{\tau}\int_0^\tau j(\xi)\cos\omega_k\xi\,d\xi \\ B_k &= \frac{2}{\tau}\int_0^\tau j(t)\sin\omega_k t\,dt = \frac{2}{\tau}\int_0^\tau j(\xi)\sin\omega_k\xi\,d\xi \end{aligned}\right\} \tag{2}$$

The following customary assumptions[1] are made regarding $j(t)$:

(A). The mean deviation from the average current, taken at the time, t over a large number of similar, but independent circuits in which the same average current flows, is zero. This is denoted by

$$\overline{j(t)} = 0. \tag{3}$$

(B). If the values of $j(t)$ are considered at different instants, t_1 and t_2, there will be correlation between successive values only when $|t_2-t_1|$ is very small. This may be expressed by the following equation:

$$\overline{j(t_1)j(t_2)} = \phi(t_1 - t_2), \tag{4}$$

where the values of $j(t)$ at t_1 and t_2 are multiplied, and the average taken again over an ensemble of circuits. $\phi(t_1-t_2)$ is a symmetric function of the difference in time with a sharp maximum at t_1-t_2 equal to zero. This will frequently be referred to as the *correlation function*. It is well known from statistical mechanics that the ensemble of currents may be formed either by a great number of independent circuits, or by dividing the curve, $j(t)$, occurring in one circuit into many sections of length τ.

We are interested now in finding an expression for the *mean square* amplitude of the kth Fourier component of the current. This may be written from the Eq. (2)

$$\overline{A_k}^2 = \frac{4}{\tau^2}\int_0^\tau\int_0^\tau \overline{j(\xi)j(\eta)}\cos\omega_k\xi\cos\omega_k\eta\,d\xi\,d\eta$$

where ξ and η are time variables of integration. Now $\cos\omega_k\xi\cos\omega_k\eta = 1/2[\cos\omega_k(\xi+\eta)+\cos\omega_k(\xi-\eta)]$ and by assumption (2) $\overline{j(\xi)j(\eta)} = \phi(\xi-\eta)$. Denoting $\xi-\eta$ by w, and $\xi+\eta$ by v, we have $dv\,dw = 2d\xi d\eta$ from the functional determinant.

Introducing these as new variables, the expression for $\overline{A_k}^2$ becomes

$$\overline{A_k}^2 = \frac{1}{\tau^2}\int_0^{2\tau}\int_{-\infty}^{\infty}\phi(w)[\cos\omega_k w + \cos\omega_k v]\,dv\,dw.$$

The extension of the limits of the integration with respect to w is justified by the steep decline of the function $\phi(w)$.

$$\begin{aligned}\overline{A_k}^2 &= \frac{1}{\tau^2}\int_0^{2\tau}\int_{-\infty}^{\infty}\phi(w)\cos\omega_k v\,dv\,dw + \frac{1}{\tau^2}\int_0^{2\tau}\int_{-\infty}^{\infty}\phi(w)\cos\omega_k w\,dv\,dw \\ &= \frac{1}{\tau^2}\int_0^{2\tau}\cos\omega_k v\,dv\int_{-\infty}^{\infty}\phi(w)\,dw + \frac{1}{\tau^2}\int_0^{2\tau}dv\int_{-\infty}^{\infty}\phi(w)\cos\omega_k w\,dw.\end{aligned}$$

Since $\omega_k = 2\pi k/\tau$, the first integral is seen to vanish at both limits, and there remains simply

$$\overline{A_k}^2 = \frac{2}{\tau}\int_{-\infty}^{\infty}\phi(w)\cos\omega_k w\,dw. \tag{5}$$

A corresponding treatment yields an identical expression for $\overline{B_k}^2$.

Correlation

In fulfilling the postulates of the normal shot effect theory, the probability of the departure of an electron from the cathode is assumed to depend only on the thermal energy of the emitter,

[1] Uhlenbeck and Ornstein, Phys. Rev. **38**, 823 (1930).

and not at all upon the previous history of the region of the surface from which it leaves. It is further assumed that the arrival of electrons at the plate partakes of the same chaotic distribution.

The situation is represented graphically in *A* Fig. 2. Under temperature limitation the number, n_i, emitted during a certain time element Δt_i all arrive during a corresponding time $\Delta t_i'$ later than Δt_i by the time of passage across the intervening space.

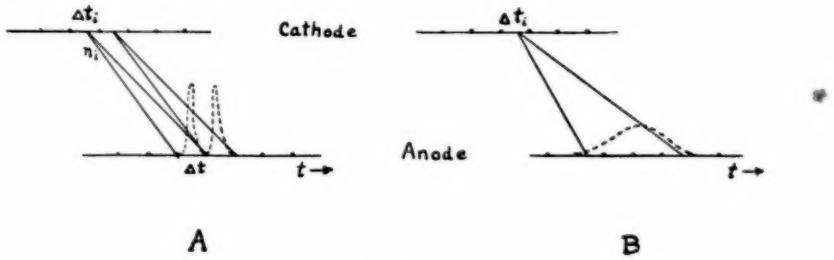


Fig. 2.

This statement has the effect of assigning an infinitesimally narrow width to the correlation function $\phi(w)$ as applied to the emission current. It follows that the integral $\int_{-\infty}^{\infty}\phi(w)\cos\omega_k w dw$ can be replaced by $\int_{-\infty}^{\infty}\phi(w)dw$ since the value of w for the range in which the integral $\neq 0$ is very small and $\cos\omega_k w = 1$. For temperature limited currents, therefore, we can write $\overline{A_k}^2 = \frac{2\sigma}{\tau}$ and an identical expression for $\overline{B_k}^2$ (6)

where

$$\sigma = \int_{-\infty}^{\infty}\phi(w)dw.$$

The application of the principles of probability to the escape of electrons from a metal surface has given for the mean square deviation from the average current $\bar{i}$

$$\bar{j}^2\Delta t = \overline{(i-\bar{i})^2}\Delta t = \bar{i}\epsilon$$

where ϵ is the charge of the electron, Δt is a time element, short by comparison with the natural period of the measuring unit, and still long enough to allow the escape of many electrons. The role played by this factor has been clearly illustrated by Huxford.[2]

This may be identified with the function $\phi(w)$ by considering that the area under the correlation curve may be approximated by a rectangle of height $\bar{j}^2$ and width Δt. Thus

$$\sigma \cong \bar{j}^2\Delta t = \bar{i}\epsilon. \tag{7}$$

The mean square amplitude of the kth component of current fluctuation,

$$\overline{A_k}^2 + \overline{B_k}^2 = \overline{C_k}^2 = \frac{4\epsilon\bar{i}}{\tau} \tag{8}$$

Adaptation of this relation to the experimental problem, and a solution applicable to all types of shot circuits have been carried out by Williams and Vincent.[3] Remembering that $\omega_k = 2\pi k/\tau$, the mean square voltage developed across the circuit load and impressed upon the amplifier becomes

$$\overline{V_k}^2 = \tfrac{1}{2}C_k^2Z_k^2 = 2Z_k^2\epsilon i_0\frac{\omega_k}{2\pi k} \tag{9}$$

It was to be expected that one of the effects of the interaction of electrons in space charge would be the "spreading" of the correlation function as applied to their arrival at the anode.

[2] Huxford, Dissertation, University of Michigan, (1928), p. 10.
[3] Williams and Vincent, Phys. Rev. **28,** 1250 (1926).

The contrast between the two types of current limitation may be depicted as shown in Fig. 2. Under extreme space charge, the emission of n_i electrons during Δt_i may influence the arrival of n_i over a considerable range of time elements, beginning nearer Δt_i than was the case, due to long range forces.

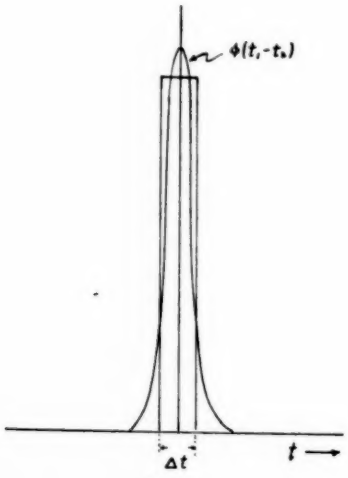


Fig. 3.

More formally, if we assign finite width to the correlation function, its value must be expressed as a symmetric, rapidly decreasing function of the difference in time between two events. This is the quantity which we have called w. An approximation which suggests itself is an exponential of the form

$$\phi(w) = Pe^{-\alpha^2 w^2/2} \tag{10}$$

where P and α are functions of the plate potential or of the space current.

Substituting this in the expression for $\overline{A_k}^2$

$$\overline{A_k}^2 = \frac{2P}{\tau}\int_{-\infty}^{\infty} e^{-\alpha^2 w^2/2}\cos\omega_k w\,dw$$

$$= \frac{2P}{\tau}\,\frac{(2\pi)^{1/2}}{\alpha}\,e^{-\omega_k^2/2\alpha^2} \tag{11}$$

for temperature limitation, we had, independent of frequency,

$$\overline{A_k}^2 = \frac{2e i_0}{\tau}. \tag{6, 7}$$

This condition is fulfilled in the space charge equation by making

$$\alpha \to \infty \text{ and } \frac{P}{\alpha}(2\pi)^{1/2} = ei$$

where i refers to the total emission or saturation current from the cathode.

It is apparent that P/α is finite and is itself a function of the space current i_0, which for $i_0 = i$ becomes $ei_0/(2\pi)^{1/2}$. Representing in general

$$\frac{P}{\alpha}(2\pi)^{1/2} \text{ by } \beta(i_0)$$

we may write

$$\overline{A_k}^2 = \frac{2\beta}{\tau}e^{-\omega_k^2/2\alpha^2} \tag{12}$$

and reasoning as before,

$$\overline{V_k}^2 = \tfrac{1}{2}Z^2C_k^2 = 2Z^2\beta\frac{\omega_k}{2\pi k}e^{-\omega_k^2/2\alpha^2}. \tag{13}$$

Then for the ratio of the mean square impressed potential fluctuation under given space charge conditions to the same quantity under temperature limitation.

$$\frac{(\overline{V_k}^2)_s}{(\overline{V_k}^2)_n} = \frac{\beta(i_0)}{\epsilon i}e^{-\omega_k^2/2\alpha^2}.$$

From dimensional considerations, we cannot escape the conclusion that the factor $\beta(i_0)/\epsilon i$ must be some function f of i_0/i which for $i_0 = i$ becomes unity. Making this substitution and denoting the depression ratio by δ, we have

$$\delta = f\left(\frac{i_0}{i}\right)e^{-\omega_k^2/2\alpha_i}. \tag{14}$$

The ratio on the left is frequently referred to in this paper simply as the *depression ratio.* Its value obviously approaches unity as strict temperature limitation is approached. For other situations indicated by the subscript s, the ratio is seen to depend on two factors, one a function of the space current and the saturation current, and the other an exponential function of the frequency.

This formal discussion of course cannot give the form of the functions α and β. For these a more detailed consideration of the mechanism is necessary. If the effect of space charge were only the spreading to which we referred, one can show that

$$\beta(i_0) = \epsilon i_0. \tag{14a}$$

The entire depression would then be caused simply by the fact that a certain fraction of the emission current is cut off by the potential minimum. A surface through the potential minimum would be considered as a virtual emitter with the same characteristics as the real cathode, but emitting fewer electrons per second. In this case also α could be determined.

One feels, however, that the spreading effect cannot be the only cause of depression. When there is space charge there will also appear fluctuations in potential due to density fluctuations of the space charge, which again is a consequence of the temperature motion. Therefore we can only expect (14a) to hold in the limit of very small depression.

Note B. Thermal Agitation

Under extreme space charge limitation, thermionic conduction is similar in many respects to metallic conduction. It has been pointed out that in this case only fluctuations due to the thermal agitation of electricity would be expected. This is analogous to the Brownian motion of particles in colloidal suspension. In an earlier section the current fluctuation was developed in a Fourier Series. We must now apply a similar development to the accidental electromotive force. Putting therefore:

$$E(t) = \sum_{k=1}^{\infty}(P_k\cos\omega_k t + Q_k\sin\omega_k t) \tag{15}$$

we find,

$$\overline{P_k}^2 = \overline{Q_k}^2 = \frac{2\rho'}{\tau} \tag{16}$$

where

$$\rho' = \int_{-\infty}^{\infty}\overline{E(t_1)E(t_2)}\cos\omega_k(t_1 - t_2)d(t_1 - t_2) \tag{17}$$

To find ρ' we must consider the differential equation of the current:

$$L\frac{di}{dt} + Ri = E(t). \tag{18}$$

The general integral is

$$i = i_0 e^{-Rt/L} + \frac{1}{L} e^{-Rt/L} \int_0^t E(t) e^{Rt/L} dt. \tag{19}$$

Squaring and taking the mean over an ensemble of currents

$$\overline{i}^2 = \overline{i_0}^2 e^{-2Rt/L} + \frac{\rho}{2RL}(1 - e^{-Rt/L}) \tag{20}$$

where

$$\rho = \int \overline{E(t_1)E(t_2)} d(t_1 - t_2)$$

which in the limit as $t \to \infty$ becomes

$$\overline{i}^2 = \frac{\rho}{2RL}. \tag{21}$$

From the equipartition of energy theorem, we have, $1/2L\overline{i}^2 = 1/2\kappa T$ where κ is the Boltzmann constant and T, the absolute temperature.

Then

$$\rho' = 2R\kappa T. \tag{22}$$

Assuming very sharp correlation, we have $\rho' = \rho$ so that

$$\overline{P_k}^2 + \overline{Q_k}^2 = \overline{V_k}^2 = \frac{4\rho'}{\tau} = \frac{8R\kappa T}{\tau} \tag{23}$$

$$\overline{V_k}^2 = 8R\kappa T \frac{\omega_k}{2\pi k} \tag{24}$$

This expression is to be compared with Eqs. (9) and (13).

It is important still to remark that we could integrate (18) also by developing i in a Fourier series in the same way as $E(t)$, and we find then for the mean square amplitude of the kth component,

$$\overline{i_k}^2 = \frac{1}{2} \frac{\overline{P_k}^2 + \overline{Q_k}^2}{R^2 + \omega_k^2 L^2} = \frac{2\rho'}{\tau R^2} \frac{1}{1 + \omega_k^2 \frac{L^2}{R^2}}. \tag{25}$$

Now, again summing over all components, we get

$$\overline{i}^2 = \sum_{k=1}^{\infty} \overline{i_k}^2 = \frac{2\rho'}{2\pi RL} \int_0^{\infty} \frac{dx}{1 + x^2} \tag{26}$$

where

$$x = \omega_k \frac{L}{R}; \quad \omega_k = \frac{2\pi k}{\tau} \quad \therefore \tau = \frac{L}{R} \cdot \frac{2\pi}{dx}$$

which gives

$$\overline{i}^2 = \frac{\rho'}{2RL}. \tag{27}$$

Comparing this with (21) we see that ρ' is necessarily equal to ρ, or that even for temperature fluctuations the correlation *must be* very sharp. The result is that for thermal fluctuations the spectrum of $\overline{V}^2$ must be uniform as in the case of the temperature limited thermionic currents. This argument now provides an *a priori* estimate of the influence of the correlation factor in the depression ratio. When in the two limiting cases, though by quite different approaches, we meet the necessity of a constant spectrum, it seems doubtful that in the transition region we would find the frequency dependence.

ON THE EQUATIONS OF LAPLACE AND MAXWELL

By Karl F. Herzfeld
Department of Physics, The Johns Hopkins University

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Abstract

An attempt is made to deduce the equations of electrostatics and of electrodynamics from general axioms instead of quantitative experiments. Among the axioms necessary to find the first are: the existence of a field, determined by differential equations without action at a distance, the principle of superposition, isotropy of space and existence of a potential. From Poisson's equation Maxwell's equations follow with four additional assumptions, the chief of which is the validity of the restricted theory of relativity.

A. Introduction

IN SEVERAL parts of physics the equations have the form of Laplace's equation or of the wave equation although the underlying mechanism is quite different. The Coulomb-Newton law of attraction, which is a consequence of Laplace's equation, holds very exactly. In a discussion back in 1911, Professor P. Ehrenfest put the question, "how exactly are Maxwell's equations fulfilled?"

Those considerations are the root of the present paper. It is an attempt to deduce, first, the equation of electrostatics in vacuum, that is Laplace's equation, then Maxwell's equations (also in vacuum) from axioms which do not contain explicit statements about the dependence of the force on the distance. J. R. Oppenheimer has pointed out that there is a remote similarity between this procedure and the one used in the general theory of relativity. We restrict ourselves to classical quantities, not matrices etc.

B. Electrostatics

I. We assume that the mechanical force per unit of volume (force-density) can be described as due to a field E, which is a vector. We do not go into the question, as to what this first assumption involves (existence of probes, conservation of charge, etc.). We have then

$$F = \rho E. \tag{1}$$

E is defined[1] by (1)

II. We assume that the field can be deduced from a potential. That means that if we move a probe on any closed curve, the work is zero and everything is back in the stage where it was when we started.

$$E = -\operatorname{grad} \phi. \tag{2}$$

[1] See however the different standpoint of W. F. G. Swann, Rev. of Mod. Phys. **2**, 243 (1930).

III. We assume that the field which is due to several charges, can be found by adding vectorially the fields (i.e., adding the potentials) which would be present if each charge were there alone. This is the principle of superposition and means that the equations must be linear in ϕ.

IV. We assume that we have a field-theory (homogeneity of space), even in the presence of charges. That means that the coordinates of the charges do not enter explicitly into the differential equations, but that the field in any place is determined microscopically only by the field in the surroundings of that place. That excludes for example an equation of the type

$$\text{div } (r \text{ grad } \phi) = 0 \qquad r^2 = (x - x_0)^2 + (y - y_0)^2 + (z - z_0)^2$$

where x_0, y_0, z_0 are the coordinates of the point-charge. The equation above would be compatible with V. Assumption IV is important, as it excludes

$$\phi = \frac{e}{r^n} \qquad n \neq 1.$$

If it were not made however, it would be difficult to see how the equations for extended charges or several point charges should be written. Probably the principle of superposition would be violated.

V. We assume that space is isotropic (has spherical symmetry). That the location of the charge does not enter into the differential equations explicitly, has already been stated in IV. It then follows that the only possible operator is the one of Laplace

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3}$$

or powers of it, if we limit ourselves to rational operators.[2] In the same way in which $r^2 = x^2 + y^2 + z^2$ (or powers of it) is the only expression invariant against rotation that holds for the operator (3).

VI. We assume that the distribution of continuous charges determines the field completely. From this it follows that the differential equations can not be of higher degree than the second, otherwise there would be superfluous constants.

Assume for example that the equation would be

$$\Delta^2 \phi = 0. \tag{3'}$$

Consider the case of one dimension, that is to say an infinite plate parallel to the $y-z$ plane, charged uniformly.

Laplace's equation has then the form

$$\frac{\partial^2 \phi}{\partial x^2} = 0 \qquad \phi = a + bx.$$

[2] $\left(\frac{\partial \phi}{\partial x}\right)^2 + \left(\frac{\partial \phi}{\partial y}\right)^2 + \left(\frac{\partial \phi}{\partial z}\right)^2$ is not linear in ϕ.

Of the two constants, a has no importance for the field while b is determined by the surface density of the charge.

(3′) however takes the form $\partial^4\phi/\partial x^4 = 0$ and has the solution $\phi = a + bx + cx^2 + dx^3$, that is to say three constants of physical importance to be determined by the single density.

The only form left is therefore

$$\Delta\phi + \frac{1}{\lambda^2}\phi = 0 \tag{4}$$

where λ is an absolute length (for dimensional reasons).

VII. If we assume that no absolute length appears in electrostatics, the second member must be absent, and we get

$$\Delta\phi = 0. \tag{5}$$

VIII. We assume that the elementary charge has spherical symmetry. That means that we can use the fundamental solution of (5), namely $1/r$, and do not need, e.g. $1/r^{n+1}\, P_n(\cos\theta)$. According to III the solution must then be e/r. If one constructs continuous charges out of point charges, one deduces easily Poisson's equation inside of the continuous charges. That the charge density ρ which appears in (1) as being acted upon and the charge density which appears here as source of the field are the same, follows from Newton's principle of action and reaction.

VIII.′ It might be interesting to see what happens if we do not make assumption VII. It is of course easy to construct a length out of absolute constants in the form

$$\lambda = k\alpha^m a_0$$

where k and m are any real numbers (k positive), a_0 the first Bohr-radius, α the fine structure constant (dimensionless). With the help of the latter it is possible to make λ as large or small as one wishes.

Then the fundamental solution is

$$\frac{e^{\pm ir/\lambda}}{r} \tag{6}$$

In (6) the imaginary exponent and in (4) $+1/\lambda^2$ has been used. Otherwise we would have had

$$\frac{e^{\pm r/\lambda}}{r}.$$

As the solution with the exponent $+r/\lambda$ is impossible under all circumstances, the differential equation with $-1/\lambda^2$ has to be excluded.

Now (6) is the spacial factor in the potential of a spherical wave of wave length λ. But then we have interference phenomena, not neutralization. I.e., if we put two equal and opposite charges at a distance $>\lambda/2$, there are directions, in which the field is stronger than it would be with a single charge. If

however λ were so great, that the fields at distances larger than λ are too weak to be measured, there would be no appreciable difference against the usual electrostatics.

C. Electrodynamics

We assume the validity of the restricted theory of relativity in a manner which will be made more precise later on.

That means that the equations must be invariant under a rotation in the four-dimensional space $x, y, z, u = i\,c\,t$.

Then the Laplace operator (3) goes over into

$$\Box = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial u^2} = \Delta - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} \tag{7}$$

We write now Eq. (1)

$$\boldsymbol{F} = \rho \boldsymbol{M} \tag{8}$$

and consider, that $\boldsymbol{F}$ is a four-vector; several theories are seen to be possible, of which only one will be worked out in detail.[3]

a. ρ can be scalar, then the field vector $\boldsymbol{M}$ is a four vector. Reasoning similarly as will be done later, a potential exists, which is a scalar

$$\boldsymbol{M} = -\nabla\phi \quad \nabla = \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial u}$$

$$\Box\phi = -4\pi\rho \tag{9}$$

That is not representative of electrodynamics, but of acoustics with longitudinal waves. Furthermore, there is no conservation of charges, because if ρ is a scalar, $e = \int \rho dx dy dz$ is not, but $e(dt/ds)$ is.

Another way in which to say the same thing is to say that the equation of continuity

$$\frac{\partial}{\partial x}(\rho v_x) + \frac{\partial}{\partial y}(\rho v_y) + \frac{\partial}{\partial z}(\rho v_z) + \frac{\partial}{\partial t}\rho = 0 \tag{10}$$

is only invariant if it is a vector equation

$$\text{Div } \boldsymbol{P} = 0 \tag{10'}$$

$$\boldsymbol{P} = \rho\frac{v_x}{c}, \quad \rho\frac{v_y}{c}, \quad \rho\frac{v_z}{c}, \quad i\rho. \tag{11}$$

b. ρ is proportional to the t-component of a four vector $\boldsymbol{P}$ (11). Then

$$\boldsymbol{F}_i = \sum \boldsymbol{M}_{ik}\boldsymbol{P}_k$$

$\boldsymbol{M}$ must be of second rank.

[3] As we restrict ourselves to the use of Cartesian coordinates, we need not distinguish between contravariant and covariant quantities. The operators are designated according to W. Pauli, Relativitatstheorie, Enz. Math. Wiss V, 19, Leipzig, 1921.

There are again two possibilities
(α) it may be a symmetric tensor

$$M_{ki} = M_{ik}.$$

One can argue again for the existence of a potential, which has to be now a four vector ϕ, satisfying Eq. (13)
M is given by

$$M_{ii} = \frac{\partial \phi_i}{\partial x_i} \quad M_{ki} = M_{ik} = \tfrac{1}{2}\left(\frac{\partial \phi_k}{\partial x_i} + \frac{\partial \phi_i}{\partial x_k}\right). \tag{12}$$

There are ten components. Three of these M_{14}, M_{24}, M_{34} are proportional to E_x, E_y, E_z respectively. Then there are seven left, four diagonals and three M_{23}, M_{31}, M_{12}. One can not put all the diagonals zero, because *that* is not invariant, but their sum is, and the number can be reduced by one.

$$M_{11} + M_{22} + M_{33} + M_{44} = 0.$$

In this way, one can throw, e.g., M_{44} out. We have then not a magnetic vector field with three components, but magnetism like elasticity would be described by a three-dimensional symmetric tensor;

$$M_{xx}, M_{yy}, M_{zz}, M_{xy} = M_{yz}, M_{zx} = M_{xz}, M_{xy} = M_{yx}.$$

(B) M_{ik} is antisymmetric; that leads to Maxwell's equation and will be discussed in detail.

c. It might be that the field $\boldsymbol{M}$ is of even higher than second rank. If it is alternating and of the third rank, that gives again a four vector (case a). If it is not alternating, there are even more components than in case bα.

Going back to a systematic enumeration of assumptions, we start out with one or more charges, which are all at rest in a certain system, in which therefore electrostatics is valid.

We now make assumption IX, that the field for an observer moving relatively to the charges is given by the transformations of the restricted theory of relativity.

Leaving open the character of ρ and $\boldsymbol{M}$ according to the hypotheses a, bα or β, one can by direct transformation of (2) show that the field can be deduced from a potential, which in case (a) is simply the scalar electrostatic potential given by (9) in case (b) a four vector given by

$$\Box \phi = -4\pi \boldsymbol{P}. \tag{13}$$

In case α the connection with $\boldsymbol{M}$ is (12), in case β it is [4]

$$\boldsymbol{M}_{ik} = \mathrm{Rot}_{ik}\Phi = \frac{\partial \Phi_k}{\partial x_i} - \frac{\partial \Phi_i}{\partial k_k} \tag{14}$$

ϕ has in this case the components A_x, A_y, A_z (electromagnetic potential) $i\phi$ (electrostatic potential).

[4] Pauli, reference 3, p. 606.

In the case of all charges at rest there is really one system which could be preferred over all others.

We take now however a case in which different charges move at different, although constant speeds.

X. We make the assumption, that the principle of superposition (linearity of $\boldsymbol{M}$ or ϕ) is valid also in electrodynamics. That does not follow from III, because there exists (in the case β) the invariant $(\boldsymbol{M}\,\boldsymbol{M}^*) = -2i(E.H)$ which disappears automatically in electrostatics, but might (in any power) appear in the equations of electrodynamics.

We can then construct the resultant field for the moving observer by adding the fields due to each charge, and as each field can be deduced from a potential, we find for a field due to any number of charges moving with arbitrary, but constant velocities, Eq. (9) or (13) with either (12) or (14), where ϕ can now not be reduced to a single quantity, namely the electrostatic potential in the rest system, as was the case in the last paragraph.

XI (a). If we require conservation of charges (10), hypothesis a and $c\alpha$ is ruled out.

XI (b). If we require the existence of a magnetic field vector, hypothesis a, and $b\alpha$ and c are ruled out, $\boldsymbol{M}$ must be antisymmetric and we have (10), (11) (13) and (14).

XII. If we make now the assumption, that IX and X remain valid even in case of acceleration and that no new vector containing properties of the electronic motion (as f.e. $\rho_0(d^2x_i/ds^2)$) appear on the right hand side of (13), Eqs. (13), (14) and (10) which are equivalent to Maxwell's equations, are the only possible ones.

D. The Question of True Magnetism

It can easily be shown, that

$$\operatorname{div} H = 0, \quad \operatorname{rot} E = -\frac{1}{c}\frac{\partial H}{\partial t}$$

are consequences of (14). Dr. O. Halpern raised the question, as to where the corresponding physical assumption had been made, and answered it himself by saying that the statement (1), which excluded magnetostatics, already contained it. A deeper investigation confirms this view.

Assume there would have been no electrostatics, but only magnetostatics and we would have had

$$F = \rho_m H. \tag{1'}$$

We would then have to introduce a univalent magnetostatic potential

$$H = -\operatorname{grad} \phi_m \tag{2'}$$

and the first part would have gone exactly as before, substituting magnetic for electric quantities. In c, we would have identified $-H$ with M_{41}^*, M_{42}^*, M_{43}^* where $\boldsymbol{M}^*$ is a six vector dual to the vector $\boldsymbol{M}$ introduced before. It

would then be possible to relate $\boldsymbol{M}^*$ to a potential $\boldsymbol{\phi}_m{}^*$ which would be a four vector, by writing

$$\boldsymbol{M}_{ik}{}^* = \mathrm{Rot}_{ik}\, \boldsymbol{\phi}_m$$

that is (with a three-vector A_m corresponding to the electromagnetic potential A).

$$H = -\operatorname{grad}\phi_m + \frac{1}{c}\frac{\partial A_m}{\partial t}$$
$$E = \operatorname{rot} A_m$$
$$\Phi_m = -iA_m, \quad -\phi_m.$$

It follows then that we have div $E=0$. Assuming then the existence of both electric and magnetic true charges, the presence of a magnetic field at rest would make it impossible to interpret the field after transformation for a moving observer as due to a single-four potential $\boldsymbol{\phi}$.

In this case,[5] the equations would have to be

$$\Box\,\boldsymbol{\phi} = -4\pi\boldsymbol{P} \qquad \Box\,\boldsymbol{\phi}_m = -4\pi\boldsymbol{P}_m \left(\boldsymbol{P}_m = i\rho_m \frac{v}{c}, -\rho_m\right)$$
$$\boldsymbol{M} = \mathrm{Rot}\,\boldsymbol{\phi} + \mathrm{Rot}^*\,\boldsymbol{\phi}_m$$
$$\mathrm{Div}\,\boldsymbol{\phi} = 0 \quad \mathrm{Div}\,\boldsymbol{\phi}_m = 0$$

which means conservation of both electric and magnetic charges.

$$\boldsymbol{F} = (\boldsymbol{MP}) + (\boldsymbol{M}^*\boldsymbol{P}_m).$$

Of course even in the absence of magnetic charges, it is possible to introduce both potentials, $\boldsymbol{\phi}$ and $\boldsymbol{\phi}_m$. But as we have then

$$\Box\,\boldsymbol{\phi}_m = 0$$

everywhere in space and want a solution which is everywhere regular, we can build up all possible solutions of this equation as superpositions of plane waves. But plane electromagnetic waves can be interpreted as well by $\boldsymbol{\phi}$ as by $\boldsymbol{\phi}_m$, so tht in this case the contribution from $\boldsymbol{\phi}_m$ can as well be considered as due to $\boldsymbol{\phi}$.

[5] There is no advantage now however in the use of the two independent potentials compared with the use of the field vectors.

SEASONAL VARIATIONS IN MAGNETIC STORMS*

By H. B. Maris
Naval Research Laboratory
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Abstract

A new list of magnetic storms for the period 1839 to 1930 has been prepared. This list represents a uniform scale of world wide disturbances for this entire period. The storms of this list show a seasonal variation in frequency with equal maxima at equinox and equal minima at solstice which follows approximately the cosine curve $y=F(3+\cos 2\theta)$ where θ is the longitude of the sun measured on the earth's ecliptic. The ultraviolet light theory of magnetic storms regards the storms as being due to three effects, gravitational ion drift currents, dynamo currents due to vertical convection and dynamo currents due to lateral winds. The first two are world wide effects and when calculated from the theory account for a little less than one third of the change in magnetic activity. The third effect is local and is estimated to account for a little over a third of the total change in activity. Accidental variations in the occurrence of non-solar magnetic storms with semiannual periods account for the remaining third of the change in magnetic storm frequency. It is to be noted that the difference between winter and summer or spring and fall activity which has previously been observed is not shown by the storms of the present list. It is concluded that annual variations in magnetic storm activity can be explained as the result of annual variations in the declination of the sun.

Introduction

SEASONAL variations in the frequency of occurence of magnetic storms have long been recognized. Sabine[1] found April and September to show about twice the activity of January and June. Writers who assumed that magnetic storms were caused by charged particles shot out from the sun in very narrow beams have sought to explain these changes by seasonal variations in the heliographic latitude of the earth.[2,3] This explanation, however, is found to be inadequate. The present paper presents the results of a critical summary of the facts of magnetic storms for the past 91 years. It shows the seasonal variation and presents a straightforward explanation based on the ultraviolet light theory of magnetic storms.

Summary of Magnetic Storms from 1840 to 1930

A new list of magnetic storms for the period 1840–1930 was prepared for use in studying periodicities in magnetic activity. This list follows approximately Maunder's[4] classification of magnitudes as shown by Table I. The magnitude of the storm is assumed to be proportional to the maximum change

* Published with permission of the Navy Department.
[1] Sabine, Phil. Trans. Roy. Soc. **141**, 123 (1851).
[2] Bauer and Duvall, Terr. Mag. **31**, 100 (1926).
[3] Cortie, Monthly Notices Roy. Ast. Soc. **73**, 57 (1912).
[4] Maunder, Roy. Ast. Soc. **65**, 4 (1904).

in hourly values of the magnetic vector during a twenty-four hour period. The unit of disturbance is $1\gamma = 10^{-5}$ gauss.

TABLE I.

Storm magnitude	Disturbance range	International Character No.	Number of storms 1840–1930
0	00–100γ	1.0 –1.5	1,463.0
1	100–200γ	1.6 –1.85	876.0
2	200–300γ	1.86–1.95	292.0
3	300–500γ	1.96–1.99	106.0
4	500– γ	2.00–	26.0

The values of disturbance range given are relative because magnitudes of disturbances at one station cannot be compared directly with the magnitudes of distrubances at another. Each station should have its own standard for storm values. A disturbance of 100γ at Cheltenham should be rated as equal to a disturbance of either 70γ at Honolulu or 250γ at Sitka. The schedule for International Character Numbers was not followed closely because they do not represent a fixed or standardized intensity of activity. No rigid mathematical rule was followed in determining the magnitude of a storm. Most storms were assigned to their respective magnitudes without question. When the rating of a storm was questionable the records of that storm for several stations were compared and the final decision was based on both the amplitude and the total activity of the disturbing forces. The total number of storms listed for each magnitude is given in the last column of Table I.

A careful effort was made to obtain a uniform scale of storm records and magnitudes for this entire period. For example, Maunder[5] lists the following storms for August 1860 which would probably be classed as one great storm by the Cheltenham classification: August 6 active; 7 active; 8 active; 9 active; 10 great; 11 active; 12 to 15 great; 16 moderate. After a comparison of this list with the hourly observations of the magnetic observatory at Prague the following storms were listed, August 7 great; 10 active; 12 active; showing three storms for the ten day period, August 7 and 16 inclusive, instead of seven as shown by Maunder or one according to the Cheltenham classification. Small disturbances directly preceding or following greater ones were omitted. Long continued disturbances were listed as one storm for each distinct maximum. Increase of activity rather than the time of beginning was taken as the time of the storm. Before a storm was listed its magnitude was determined by a comparison of the records of several widely separated stations whenever such a comparison was possible.

The storm list as finally completed represents a comparative study of storm records from the following observatories; Prague, Toronto, Greenwich, Colaba, Cheltenham, Sitka, Honolulu, Mauritius and Dansig. The records of these observatories were compared with the magnetic storm lists prepared by Airy[6] and Maunder[4,5] and the records of International Disturbed Days, as

[5] Maunder, Monthly Notices, Roy. Ast. Soc. **65**, 540 (1905).
[6] Airy, Phil. Tran. **153**, 617 (1863).

shown in Table I, from Charactere Magnetique, DeBilt. The final list as shown in Table I contains 2763 disturbances of which 1300 were of sufficient intensity to be classed as storms of intensity 1 or greater. The remaining 1463 disturbances, too small to be classed as storms, were included in the list for future studies, in the present paper we confine our attention to the 1300 storms. These were plotted with frequency of occurrence as ordinate and time of the year as abscissa in curve 1, Fig. 1. The curve has been smoothed by plotting for each five day interval one half the number of storms for that interval plus one fourth the number of storms for the preceding and succeeding five days. This observed frequency curve shows approximately, equal maxima at the equinoxes and equal minima at the solstices. Bauer and Duvall,[2] Graetz[7] and Cortie[8] found the spring maximum greater than that of the fall and the summer minimum greater than that of the winter; there is only

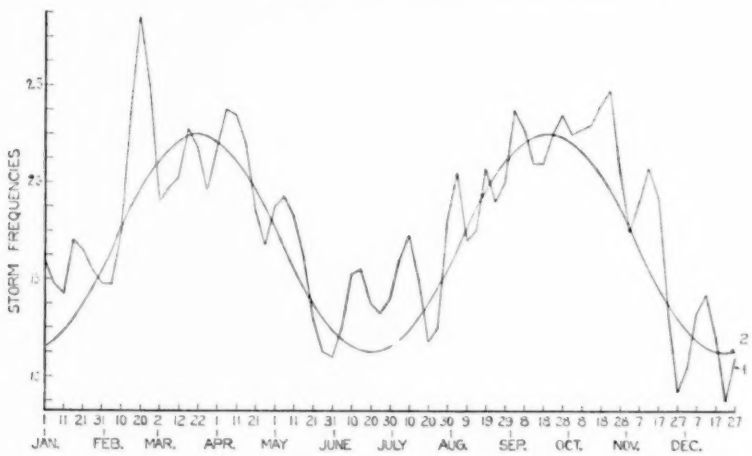

Fig. 1.

slight evidence of these changes in curve 1. The greater symmetry of curve 1 probably is the result of the different method and longer period of time used in preparing the table of storms from which it was plotted. The period, 91 years, is much longer than the time used for any previous table of storms and each storm in the table represents a world wide disturbance. Most of the previous lists of storms were based on the records of only one observatory.

Solar and Non-solar Storms

Curve 1 is quite symmetrical as a whole and follows approximately a cosine curve 2, Fig. 1, with the maximum equal to double the minimum where F

$$y = F(3+\cos\ 2\theta)$$

is an empirical constant and θ is the longitude of the sun on the ecliptic. Departures from this curve are however far too great to be considered as accidental variations; moreover these departures are to a certain extent system-

[7] Graetz, Handbuch der Elektrizitat und des Magnetismus **4,** 1095 (1920).
[8] Cortie, Mo. No. Roy. Ast. Soc. **73,** 57 (1912).

atic. A large group of storms in the first half of the year is often followed by another group six months later showing a semiannual period of return for the storms of the groups. Examples of the semiannual period are shown in Fig. 1 by the February 20 and August 19 groups and also by the May 11 and November 12 groups. Additional proof that the storm groups are not accidental is given by the fact that the storms which make up the groups often show quite definite relations to each other. Storms of the February 20 group first appeared in 1840 with a series of storms which started January 31, included a 4 storm February 7 and lasted until February 15. This series was repeated on identical dates in 1841. The group gradually decreased in intensity until 1880 and has not appeared since then. Storms of the May 11 group began to appear with a 4 storm November 17, 1882 and have continued up to the present, appearing in both May and November in 1931. A third group of storms began to appear April 9, 1858 with a 3 storm and has appeared intermittently since then.

Of the 26 very great storms listed in Table I all but two are apparently associated with one of the three semiannual groups given above. Greaves and Newton[9] found that the very great storms did not belong with those magnetic storms which showed a tendency to recur after a 27 day interval. We can now say they do belong to groups of storms with semiannual periods. A more complete study of the storms with semiannual periods of recurrence will be made in a later paper. For the present, it is sufficient to call attention to the fact that there are two types of magnetic storms, one apparently of non-solar origin with a semiannual period and another of solar origin with a 27 day period. The ultraviolet light theory of magnetic storms deals of course, only with the storms of solar origin which include about 3/4 of the total number. Curve 1 represents a summation of storms of both types. It is not possible to separate one type of storm from the other but it seems probable that if storms with semiannual period could be eliminated the change in frequency from solstice to equinox would be reduced by perhaps 30 percent or from 1/2 to 1/1.7.

Narrow Beam Theory

Cortie and also Bauer and Duvall have suggested that the annual changes in storm frequency could be explained by changes in the heliographic latitude of the earth as viewed from the sun. The axis of rotation of the sun makes an angle of 7.1° with the normal to the earth's orbit and an observor on the sun would see the earth move north and south across the sun's equator much as we see the seasonal movements of the sun. Variations in heliographic latitude the earth might cause the observed seasonal changes in storm frequency if the disturbance which caused a storm moved out from the sun in a narrow beam which decreased to one fourth its maximum intensity in a spread of 7°. The observed relation between comet activity and magnetic storms[10,11] has shown

[9] Greaves and Newton, Mo. No. Roy. Ast. Soc. **89,** 641 (1929).
[10] Maris and Hulburt, Phys. Rev. **33,** 1058 (1929).
[11] Maris, Trans. Amer. Geo. Union, p. 131 (1931).

that the disturbance creating a storm moves out from the sun in a widebeam comparable with the distribution of energy radiated from a flat surface. The narrow beam hypothesis is, therefore untenable. When we consider the problem of a restricted beam the known close relation between the 11 year cycles for sun spots and magnetic activity would lead us to expect storm disturbances from latitudes on the sun where sun spots are most frequent, from $\pm 10°$ to $\pm 20°$. If we assume a beam which varies in intensity as the cosine of twice the angle of departure from the maximum, from latitude $+15°$ on the sun, the decrease in intensity as the earth moves from maximum to 0° latitude will be about 10 percent, but since a similar beam from $-15°$ solar latitude would increase in intensity by about 16 percent during this change the net change in solar activity would be an increase of 3 percent. Although we have assumed a beam narrower than that indicated by the comet activity we find the change in solar activity accompanying changes of solar latitude the reverse of that required to explain the seasonal variation in magnetic storm frequency.

Ultraviolet Light Theory

The average magnetic storm is made up of three parts two of which are world wide while the third is local. The first impulse of a storm is marked in the lower latitudes by a very sudden increase in the strength of the horizontal component of the earth's field. This is followed by a much slower and much greater decrease in strength for the same component after which there is a gradual return to normal field strength. These activities constitute what we may think of as the first two, or the world wide, phases of the storm. The amplitudes of these changes are approximately independent of latitude. Superimposed over the later part of the world wide activities there is generally a series of local disturbances which vary greatly in amplitude throughout the day. These disturbances center in the polar regions and generally show a decrease of 1/5 to 1/10 in amplitude between latitudes 50 and 30 degrees. We will speak of these local disturbances as the third phase of the magnetic storm. Individual storms of course show all possible combinations of these three different phases. Some storms show very little local disturbance while in others it is almost impossible to detect anything of the world wide effect. Local disturbances may be delayed as much as 48 hours in passing from one part of the globe to another.

The ultraviolet light theory[12,13] of terrestrial magnetic storms assumes that a sudden increase in the ultraviolet radiation of the sun produces an immediate increase in the density of ionization of the earth's upper atmosphere. Ion drift currents resulting from the combined action of the earth's gravitational and magnetic field produce the first impulse of the magnetic storm. Motions of the conducting regions of the atmosphere which result from the rapid heating associated with increased absorption of ultraviolet light have a dynamo effect which furnishes energy for later phases of the storm.

[12] Maris and Hulburt, Phys. Rev. **33,** 412 (1929).
[13] Hulburt, Phys. Rev. **36,** 1560 (1930).

First Phase of Magnetic Storm

The first phase of a magnetic storm is proportional to the magnetic moments of the ion drift currents that cause it, which is given by the expression

$$S = K \int_{-90}^{+90} I \cos^2 \omega d\omega \tag{1}$$

where S is the magnetic activity, ω is the geographic latitude, I is the ion drift current flowing along the parallel of geographic latitude and K is a constant. The value of this current flowing for any given latitude is

$$I = Dew \tag{2}$$

where D is the number of long free path ions per cm² vertical column and w is the magnetic gravitational drift velocity. W is given by the relations.[14]

$$W = mgA/H_0e, \tag{3}$$

and

$$A = \cos \phi/(1 + 3 \sin^2 \phi) \tag{4}$$

where H_0 is the strength of the earth's magnetic field at the equator, m is the mass and e the charge of the ion, g is the acceleration of gravity and ϕ is the magnetic latitude. From 1, 2, 3, and 4 we have,

$$S = \frac{Kmg}{H_0} \int_{-90}^{+90} AD \cos^2 \omega d\omega. \tag{5}$$

Average values for A and ϕ for the different geographic latitudes, based on the assumption that magnetic latitude is symmetrically distributed about a pole 20° from the geographic pole, were obtained by calculating values of the magnetic functions along the given parallel for each 30° of longitude and taking the average of these calculated values. Columns 2 and 3 of Table II

Table II.

Geograph. latitude	A	A averaged	D/D_0 Equinox	D/D_0 Solstice Winter	D/D_0 Solstice Summer	M/M_0 Equinox	M/M_0 Solstice Winter	M/M_0 Solstice Summer
90°	1.0	0.835	1.0	0.920	0.920	0.100	0.920	0.920
80	0.903	0.804	0.985	0.839	0.974	0.922	0.785	0.911
70	0.695	0.701	0.940	0.731	0.999	0.690	0.538	0.736
60	0.494	0.553	0.866	0.602	0.993	0.430	0.299	0.497
50	0.342	0.405	0.766	0.454	0.956	0.219	0.128	0.274
40	0.233	0.288	0.643	0.292	0.891	0.092	0.042	0.127
30	0.154	0.198	0.500	0.122	0.799	0.029	0.007	0.047
20	0.092	0.133	0.342		0.682	0.006		0.013
10	0.045	0.103	0.174		0.545	0.001		0.002
						5.808		5.333

give respectively the original and the averaged values of A for the latitudes shown in Column 1. Columns 4, 5 and 6 give values of D/D_0 where D_0 is the

[14] Hulburt, Phys. Rev. **34**, 1167 (1929).

value of D at noon on the equator during equinox and columns 7, 8 and 9 give relative values of the magnetic moments of I calculated by means of equation 5. These values are plotted in the curves of Fig. 2 where E represents equinox and S solstice conditons. The area under each curve is proportional to the magnetic effect of ion drift currents for the time of year it represents. Denoting these areas by S_e and S_s, respectively, we have

$$S_e/S_s = 5.81/5.33 = 1.09.$$

Therefore the magnetic moment of the drift currents at equinox is 9 percent greater than at solstice and since the first phase of a magnetic disturbance is proportional to these moments we would expect magnetic storms at equinox to be about 9 percent greater in their first phase than those at solstice. A rough check of Cheltenham magnetic records shows this to be a fact.

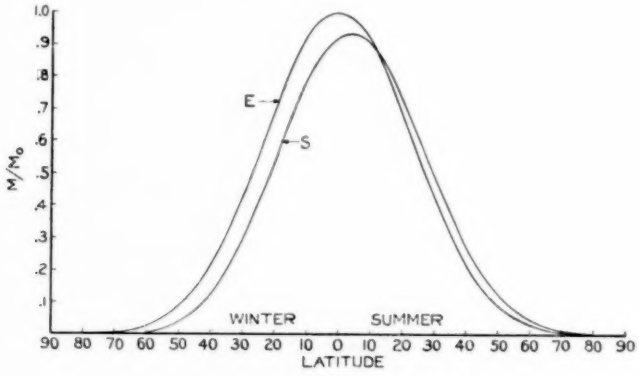

Fig. 2.

Second Phase of Magnetic Storm

Expansion of the atmosphere due to heating during a solar ultraviolet outburst will produce short lived vertical air movements which may reach a velocity of 30 kilometers per hour or more at altitudes greater than 120 kilometers. Following the vertical displacements, horizontal winds will develop which may blow with very great velocities. These winds blowing across the earth's magnetic field give rise, in the short free path region of the atmosphere, to electric currents which will create local disturbances in the earth's magnetic field proportional to the magnetic moments of the currents flowing.

Vertical air movements may be assumed to provide energy for the second phase of a magnetic storm. The magnitude of the disturbance S will again be given by Eq. (1). Where I the atmospheric current has replaced the ion drift current in the equation. The currents are assumed to flow along parallels of latitude and the current I along any particular parallel is driven by the electromotive force E of all the vertical wind along that parallel in opposition to the resistance R of the entire circuit of the parallel.

$$I = E/R. \tag{6}$$

The total electromotive force E for any parallel of latitude is equal to the sum of the electromotive forces along the parallel. The local electromotive force for any small section dx of the parallel is equal to $HV\,dx$, where H the horizontal component of the earth's field is a constant, V the velocity of vertical air motion varies with the longitude from sunrise to sunset, and dx the distance along the parallel is equal to $(\cos\omega/r)d\alpha$. ω is the latitude, r is the radius of the earth and α is the longitude. We have then

$$E = H\int_{\text{sunrise}}^{\text{sunset}} (V\cos\omega/r)d\alpha \tag{7}$$

H the horizontal component of the earth's magnetic field is equal to $H_0\cos\phi$, ϕ being the magnetic latitude corrected for wabble of the magnetic pole and H_0 being the strength of the earth's field at the equator. The velocity of vertical air motion is assumed to be proportional to the intensity of the radiation which creates it or, $V = k\cos\beta$, where β is the angle the sun makes with the zenith. Since the length of the sunlit path is proportional to $\cos\beta$ at noon an approximate solution of 7 sufficiently accurate for our use is given by the expression

$$E/E_0 = \cos\phi\cos{\beta_0}^2 \tag{8}$$

where E_0 is the electromotive force developed at the equator during equinox. β_0 is the angle of the sun at noon. From 6, 7 and 8 we get the following relation for magnetic storm activity at solstice and equinox

$$\frac{S_e}{S_s} = \frac{\sum_{-90}^{+90}\sigma\cos\phi\cos^2\omega\cos^2\beta_e}{\sum_{-90}^{+90}\sigma\cos\phi\cos^2\omega\cos^2\beta_s} \tag{9}$$

where β_s and β_e are the noon angles of the sun at solstice and equinox and σ the conductivity is $1/R$.

Table III and IV give the summations for a solution of Eq. (9). Column 1 gives the latitude and column 2 the relative resistance R_0/R where R_0 is the resistance of the equatorial circuit at equinox and R is taken from Fig. 5 of Hulburt's calculations.[15] These values are plotted against the latitude in Fig.

TABLE III. *Solstice.*

Latitude ω	R_0/R	$\cos\phi$	$\cos^2\beta$	$\cos^2\omega$	M/M_0
73	1.50	0.375	0.413	0.085	0.020
63	1.52	0.507	0.587	0.206	0.093
53	1.45	0.639	0.750	0.362	0.253
43	1.35	0.753	0.883	0.535	0.480
33	1.25	0.848	0.970	0.704	0.724
23	1.11	0.925	1.00	0.847	0.870
13	0.950	0.975	0.970	0.9494	0.852
3	0.696	0.998	0.883	0.997	0.611
7	0.508	0.994	0.750	0.985	0.376
17	0.330	0.958	0.587	0.914	0.170
27	0.269	0.897	0.413	0.794	0.079
37	0.216	0.812	0.250	0.638	0.028
47	0.168	0.708	0.117	0.465	0.006
					45.62

[15] Hulburt, Phys. Rev. **35**, 243 (1930).

TABLE IV. *Equinox.*

Latitude ω	R_0/R	$\cos \phi$	$\cos^2 \beta$	$M/M_0^{\frac{1}{2}}$
0	1.00	1.00	1.00	1.00
10	0.940	0.986	0.970	0.874
20	0.790	0.944	0.883	0.582
30	0.655	0.875	0.750	0.322
40	0.503	0.784	0.587	0.136
50	0.402	0.677	0.413	0.047
60	0.331	0.550	0.250	0.011
70	0.337	0.413	0.117	0.002
				49.48

3 where the curve E shows resistance for equinox and S for solstice. Column 3 gives the cosine of the magnetic latitude averaged for wabble of the magnetic

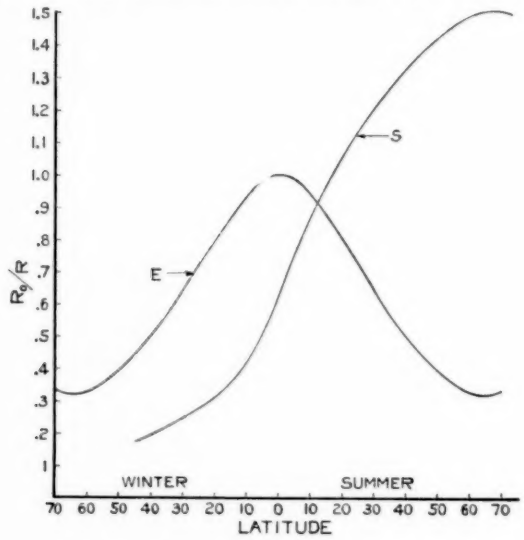

Fig. 3.

pole. Column 4 gives the square of the cosine of the sun's angle at noon and column 5 the square of the cosine of the geographical latitude. Column 5 being identical with 4 is omitted from Table IV. The last column gives values of $I/I_0 \cos^2 \omega$ where I is the electric current flowing through the atmosphere at the latitude given in column 1 and I_0 is the current which flows at the equator during equinox. These values plotted in Fig. 4 give in the area under the two curves, the solution of Eq. (9) $Se/S_s = 4.948/4.56 = 1.09$ which shows that the second phase of a magnetic storm is 9 percent greater at equinox than at solstice.

MAGNETIC STORM LOCAL CHANGES

The world-wide components of a solar magnetic storm, which were the only ones considered in the above calculations, include less than half of the total energy of the storm. The remainder of the energy is involved in local disturbances of the magnetic field which are probably caused by horizontal

winds in the conducting layer of the upper atmosphere. At the present time it is not possible to make an estimate of seasonal changes in these winds, but they would reach a maximum at equinox when the noon temperature change from the equator to either pole would be a maximum. It seems probable that seasonal changes in these winds at great altitudes contribute a large factor in determining seasonal changes in the frequency of magnetic storms. It should be pointed out in discussing the magnetic effects of winds at great altitudes that these winds probably have a world wide symmetry during magnetic quiet days when the velocities attained are not great, but they probably consist of a large number of local turbulent activities during days of magnetic storm. We should picture these upper atmosphere storms as being very similar to the tornadoes, cyclones and hurricanes in the lower atmosphere. The velocities developed may be much greater than any developed at sea level but just as in the lower atmosphere the extent of any one turbulence is prob-

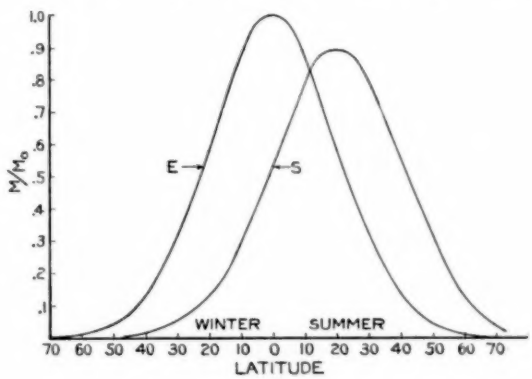

Fig. 4.

ably confined to a radius of a few hundred or perhaps a thousand miles. These upper atmosphere storms apparently require three or four hours to develope and spend their force in about the same time.

Seasonal Variations in Magnetic Activity

The seasonal increase in magnetic storm frequency from solstice to equinox shown in Fig. 1 should be considered as due to three causes. Accidental variations in the distribution of non-solar storms accounts for about one third of the change. The distribution of these non-solar storms has changed completely several times during the ninety year period of the study. Therefore, we conclude the distribution is accidental. Since they have a semiannual period it is obvious their distribution will be very effective in warping the seasonal frequency curve with its semiannual period. It is felt that the assigning of one third of the frequency change to this cause is a conservative estimate. A comparison of the second and last colums of Table I shows that a 9 percent increase in storm intensity would ordinarily result in a 9 percent increase in storm frequency. It is not certain that the increases calculated for the world wide components of a magnetic storm are additive but it seems

probable that they are. If this is true, then the world wide components of the storm would according to the calculations account for a little less than a third of the total frequency change. The remainder of the frequency change which amounts to a little more than a third of the whole can be explained as due to seasonal variations in the local disturbance effect of magnetic storm. We have thus accounted for the entire frequency change from solstice to equinox, one third is observed to be due to non-solar storms, a little less than a third is calculated to be due to changes in the world wide component of solar storms and a little over a third is estimated to be due to seasonal changes in the local magnetic effects of winds in the conducting regions of the atmosphere.

A PRECISION METHOD FOR DETERMINING THE THERMAL DIFFUSIVITY OF SOLIDS

By Richard H. Frazier
Massachusetts Institute of Technology

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Abstract

The method described utilizes a transient heat-flow phenomenon requiring the measurement only of time interval and a quantity proportional to temperature difference. The theory of the method is fully developed, and apparatus and procedure for meeting the conditions of the theory are described, together with methods for eliminating and minimizing errors. The results of a test on a nickel specimen are given, showing a precision of about 0.1 percent.

I. Introduction

IN ANALYSING a proposed method for the determination of the Thomson effect[1] in metals, it became evident that certain physical constants of a metal under consideration needed to be known with a precision of about 0.5 percent. An investigation of standard tables soon indicated that these constants were not available to this degree of precision, and that for thermal conductivity and specific heat in particular there did not appear to be in existence methods of determination reliable to the degree of precision desired. In the case of electrical resistivity, though precision methods exist, the usefulness of tabular data is voided for precise work because there is no accompanying correlation with respect to the degree and nature of impurities in the nominal material, nor with the internal structure as determined by the process of manufacture. Hence, though individual determinations may be of high precision, the test specimens always contain traces of impurities and sometimes very appreciable amounts; yet frequently no chemical analysis or other descriptive matter accompanies the data. Since the chemical and physical condition of the material influences also the thermal conductivity, though in general probably to a smaller extent, and the specific heat, though in general probably to a much smaller extent than the electrical resistivity, the same uncertainty is present in the use of tabular data for these thermal constants, in addition to their greater lack of precision. In some tables the data are averages derived from the results of a large number of experimenters.[2] Even for

[1] To be followed up in the near future.

[2] For example, in the International Critical Tables values for specific heats are given to four figures with a temperature correction coefficient of three figures, all figures in bold-face type. The following explanation accompanies the table: "Values in bold-face type are best' values deduced from all information available. The accuracy of these values is difficult to estimate, but, in general, it may be stated that specific heat data on metals are rarely accurate to better than 1%, an uncertainty of several % being not unusual." For thermal conductivities a "most probable" value is given together with a range of as much as 10 percent within which the "true" value is supposed to lie.

moderately precise work, therefore, it is necessary to determine these quantities directly upon the specimens concerned.

The experimental method outlined in this paper enables the precise determination of the thermal diffusivity, i.e., the ratio of the thermal conductivity to the product of specific heat and density. Since density can be determined to a high degree of precision, there remains the necessity for determining with precision either the thermal conductivity or the specific heat in order to make both available.[3]

II. Theory

One of the chief difficulties in thermal measurements is the precise determination of quantity of heat flow. The feature of the present method is that it avoids this measurement by utilizing a transient phenomenon[4] in which it is necessary to measure only time interval and a quantity proportional to temperature difference, both of which can be obtained with precision. In fact no temperature calibration is needed other than an approximate one as a matter of secondary interest.

If a rod of uniform cross section initially in thermal equilibrium has the temperature at one end suddenly changed to and maintained at a slightly different temperature, the subsequent change in temperature distribution along the rod is given by

$$\Delta T_x = \Delta T\left\{1 - \frac{4}{\pi}\left(\epsilon^{-pt}\sin\frac{\pi x}{2L} + \frac{\epsilon^{-9pt}}{3}\sin\frac{3\pi x}{2L} + \frac{\epsilon^{-25pt}}{5}\sin\frac{5\pi x}{2L} + \cdots\right)\right\} \quad (1)$$

where ΔT_x = change in temperature at distance x from the end where the temperature is changed, ΔT = impressed temperature change, t = time measured from the instant of change of temperature, $p = k\pi^2/4c\rho L^2 = \alpha^2\pi^2/4L^2$, k = thermal conductivity, c = specific heat, ρ = density, L = length of rod; provided that the flow of heat is linear, parallel to the axis of the rod and that there is no loss or gain of heat other than from the end at which the temperature change is impressed.

The temperature difference between two points a and b on the rod is represented by

$$\Delta T_a - \Delta T_b = \frac{4}{\pi}\Delta T\left\{\epsilon^{-pt}\left(\sin\frac{\pi b}{2L} - \sin\frac{\pi a}{2L}\right) + \frac{\epsilon^{-9pt}}{3}\left(\sin\frac{3\pi b}{2L} - \sin\frac{3\pi a}{2L}\right) + \frac{\epsilon^{-25pt}}{5}\left(\sin\frac{5\pi b}{2L} - \sin\frac{5\pi a}{2L}\right) + \cdots\right\}. \quad (2)$$

By proper selection of L all harmonics beyond the third can be made to damp out rapidly, and the third harmonic can be eliminated, or very nearly so, by selecting a and b so that

[3] A method for the precise determination of specific heat is now being worked upon.

[4] L. R. Ingersoll and O. A. Koepp have determined thermal diffusivities of certain soil materials by a procedure involving the same principle as is the basis of this method. "Thermal Diffusivity and Conductivity of Some Soil Materials", Phys. Rev. **24,** 92 (1924).

$$\sin\frac{3\pi b}{2L} = \sin\frac{3\pi a}{2L}, \tag{3}$$

or very nearly so. With the third harmonic eliminated, the equation may be written

$$\frac{\Delta T_a - \Delta T_b}{\Delta T} = A\epsilon^{-pt} + B\epsilon^{-25pt} + \cdots, \tag{4}$$

or after a moderate interval

$$\frac{\Delta T_a - \Delta T_b}{\Delta T} = A\epsilon^{-pt} \tag{5}$$

very nearly, A, B, etc., being new constants each depending on a, b and L.

If the rod is of metal, the temperature difference between points a and b can be utilized to generate an electromotive force in a thermocouple by soldering a fine wire of metal different from the rod into a small hole drilled at a, and a similar wire into a hole drilled at b, the rod itself thus constituting an element of the thermocouple.

If the thermocouple circuit is closed through a galvanometer, the motion of this galvanometer during the thermal transient can be analysed on the following assumptions: (1) that the flow of current in the thermocouple circuit does not affect the temperature difference between a and b, (2) that the electrical resistance of the thermocouple circuit does not change, and, (3) that no extraneous electromotive forces exist in the circuit. The differential equation of motion is

$$P\frac{d^2\theta}{dt^2} + k'\frac{d\theta}{dt} + \tau\theta = Ci \tag{6}$$

where P = moment of inertia of suspended parts, θ = angular deflection from position of rest, k' = damping constant, exclusive of electromagnetic damping in the circuit, τ = torsional constant, C = coil constant, i = current in circuit.

If the further assumption is made that the inductance of the circuit is zero, the current can be expressed,

$$i = \frac{e_t - e_g}{r} \tag{7}$$

where e_t = electromotive force of thermocouple, e_g = electromotive force due to motion of galvanometer, and r = total circuit resistance. But since

$$e_g = C\frac{d\theta}{dt}, \tag{8}$$

the equation of motion can be written

$$P\frac{d^2\theta}{dt^2} + \left(k' + \frac{C^2}{r}\right)\frac{d\theta}{dt} + \tau\theta = D(\Delta T_a - \Delta T_b), \tag{9}$$

D being a constant depending upon the metals of the thermocouple.

The damping "constant" k' is not strictly constant but very nearly so[5] since it takes into account air damping, internal friction in the suspension and lower helix and other possible stray sources; but unless the galvanometer is much under-damped these are so small in comparison with the electromagnetic damping of the circuit that it is permissible to call

$$K = k' + \frac{C^2}{r} \tag{10}$$

a constant. The solution of the equation of motion then is, inserting the series form of the right-hand member,

$$\theta = M\epsilon^{-mt} + N\epsilon^{-nt} + Q\left\{\frac{A\epsilon^{-pt}}{(p-m)(p-n)} + \frac{B\epsilon^{-2t/5}}{(25p-m)(25p-n)} + \cdots\right\} \tag{11}$$

where

$$\begin{aligned} m &= \frac{K}{2P} + \left(\left(\frac{K}{2P}\right)^2 - \frac{\tau}{P}\right)^{1/2} \\ n &= \frac{K}{2P} - \left(\left(\frac{K}{2P}\right)^2 - \frac{\tau}{P}\right)^{1/2} \end{aligned} \tag{12}$$

and M, N and Q are constants depending on the impressed temperature change and the sensitivity of the galvanometer, and in the case of M and N upon the initial conditions.

If the proportions of the apparatus are so selected that m and n are very large in comparison with p, and so that none of the denominators of the terms of the series can become zero, the first two terms of Eq. (11) will vanish very rapidly, and the terms of the series beyond the fundamental will vanish substantially as for the temperature-difference equation, so that after a moderate interval,

$$\theta = \frac{QA\epsilon^{-pt}}{(p-m)(p-n)} = R\epsilon^{-pt} \tag{13}$$

very nearly. It is evident therefore that even though the curve of galvanometer deflections against time converted by the proper calibration factor for the sensitivity of the instrument does not correspond point for point with the thermal curve, the two curves have the same decrement after a moderate interval, so that it is necessary merely to determine p from the curve of galvanometer deflections.

III. Apparatus and Procedure[6]

The temperature impulse is obtained by suddenly subjecting one end of the specimen to a stream of cold water. The arrangement for this for a nickel

[5] See Laws' "Electrical Measurements", p. 25.

[6] A number of schemes which were tried but discarded due to inherent difficulties in construction of apparatus or in making observations are not mentioned here due to lack of space. Complete data are on file.

specimen is shown in Fig. 1. The exposed end of the specimen is sweated into a thin flanged collar also of nickel. This flange is soldered to the top of a thin nickel tube surrounding the specimen and slightly longer. The bottom of the tube is closed by a nickel disk. The top of the nickel tube is expanded and soldered into a nickel disk which in turn rests upon and is soldered to a shoulder in an outer nickel tube, longer than the inner one. The stream of water passes over the top surface of the specimen and disk but cannot penetrate below that level.

The space between the tubes and the specimen below the disk is evacuated. The surfaces of the specimen and tubes are polished. The tubes being

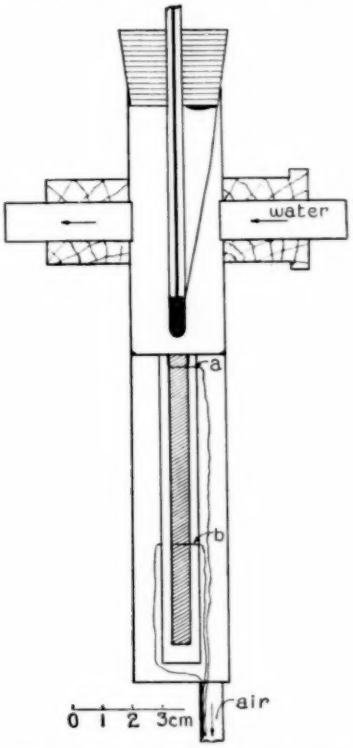


Fig. 1. Section through specimen.

of the same material as the specimen and of nearly the same length below the water have nearly the same temperature distribution (especially the inner tube) as the specimen and consequently constitute thermal guards. These arrangements result in reducing the loss or gain of heat by the specimen other than from the top surface to a negligible amount, and hence in attaining substantially linear heat flow.

At *a* and at *b* on the specimen is soldered a fine copper wire extending through the specimen in a small hole. Outside the specimen these wires aer enamel-covered. Each is led through a small hole in the inner tube directly opposite the point of junction with the specimen, wrapped once around the tube and attached to the tube by shellac. The wires are then led out through the vacuum hose to the galvanometer.

The complete apparatus is shown diagrammatically in Fig. 2. The deflections of the galvanometer are observed by means of a telescope and scale. The time at which predetermined scale divisions are reached is recorded on a chronograph the time standard for which is established by a calibrated pendulum. The fifth harmonic of the temperature difference-time curve for this specimen becomes negligible after 60 seconds have elapsed, and the higher harmonics become negligible sooner.[7] By the method of least squares an exponential curve is fitted to the galvanometer deflections taken subsequent to this time and p determined therefrom.

Though in theory the procedure is almost ideal, in practice there were certain errors which had to be eliminated or compensated for in order to preserve the precision.

The most troublesome of these errors was due to elastic fatigue in the galvanometer suspension and lower helix. A number of different galvanometers were tried and many combinations of suspension and lower helix of different materials, lengths, and cross-sections before a combination was found which had a very good straight-line characteristic for deflections read at the proper time after closing the galvanometer circuit, and which also had a fatigue effect less than 0.5 percent of full scale deflection and so consistent that it could be corrected for with precision. As a basis for the corrections, a series of up-scale deflections were taken, the readings being made at such intervals after closing the galvanometer circuit as (in accordance with the amount of damping) should be required for the galvanometer to come within 1/10,000th part of its ultimate deflection. This interval was about 6 seconds, while the further deflection due to elastic fatigue required several minutes. The galvanometer then was put through approximately the same cycle as caused by the thermal transient by means of the dropwire test circuit, Fig. 2. The differences between corresponding down- and up-scale readings constituted the corrections. A number of such tests were made, some intermingled with the diffusivity runs. The results of these showed a maximum average deviation from straight line for the up-scale deflections of about 1 part in 2000, and a maximum probable error for the corrections of about 0.005 cm. The scale reading could be estimated to 0.01 cm or about 1 part in 1000 to 4500 according to the size of the reading, so that the probable error of the corrections and the deviation of the current sensitivity from a constant value were within the range of uncertainty of estimating the galvanometer readings.

In order further to preserve the validity of the readings, corrections were made to allow for the flatness of the scale by making use of the relation

$$280(\tan\theta - \theta) = 280\left(\frac{\theta^3}{3} + \frac{2\theta^5}{15} + \cdots\right), \tag{14}$$

280 cm being the scale distance. Since there were practically no errors due to

[7] For the apparatus now in use the location of the junctions is such that $(\pi a/2L) = 0.0523$, or 3° and $(\pi b/2L) = 0.995$, or 57°. For the apparatus on which the results reported herein were obtained the corresponding figures were 5° and 60° which introduced a small third harmonic and necessitated a larger interval prior to the taking of useful observations.

mechanical vibration of the galvanometer during the runs, it may be said that except for the smaller deflections near the ends of the runs, the individual corrected readings could be considered reliable within 1 part in 1000 or better.

The pendulum was calibrated to 1 part in 20,000. The chronograph pencils were adjusted by placing their operating coils in series and regulating for simultaneous operation. There was of course a certain time lag in the operation of the pencils subsequent to the closing of their operating-coil circuits, but since the same lag was present in each motion of each pencil, there was no resulting error. The chronograph could be read to 0.01 second which probably was considerably shorter than the reaction time of the observer. This time however is of negligible consequence unless it should vary greatly.

Since some 25 to 30 useful readings were made for each run, extending over a period of about 4 minutes, it is seen that the precision with which the deflection and time for each point can be determined permits the most probable exponential curve represented by the points to be located with a degree of precision much higher than that of the individual points.

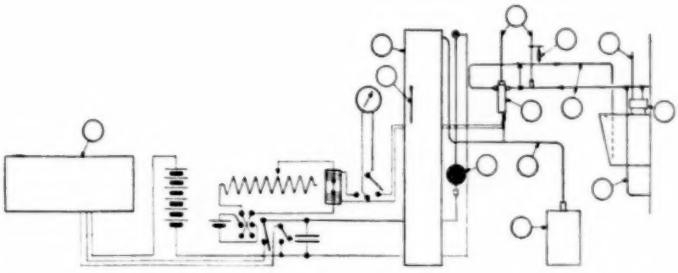


Fig. 2. Diagram of apparatus. 1, Water pipes; 2, Compressed air pipe (for blowing out water after run); 3, Water trap; 4, Thermometers; 5, Magnifying glass; 6, Specimen; 7, Glass tubing, vacuum system; 8, Vacuum pump; 9, Pendulum; 10, McLeod gauge; 11, Chronograph.

In addition to investigating the precision with which the individual readings can be made, it is necessary to investigate how well the conditions demanded by the theory are represented.

It is essential to have the specimen in thermal equilibrium before starting a run. This was checked until the temperature difference between junctions on the specimen was less than 0.001°C, the impressed temperature change being about 5°C. The galvanometer was checked on short circuit before and after each test for internal thermoelectric effects.

The theory calls for no loss or gain of heat by the specimen except through the exposed end. The temperature difference between the inner guard tube and the specimen was determined by means of several auxiliary junctions located on the guard tube. Calculations based on these differences showed that by the most pessimistic assumptions the losses by radiation, conduction through air and the thermocouple leads could not exceed 0.07 percent of the change in heat content of the specimen during the run, and probably were more nearly of the order of 0.01 percent. The vacuum of 1 micron needed to

reduce air conduction to the amount involved in this calculation was checked by means of a McLeod gauge before and after each run.

The theory also calls for an instantaneous change in temperature at the top end of the rod and a steady temperature thereafter. Since such conditions are impossible to attain absolutely on account of the necessity of a small temperature drop in the water, the question arises as to how closely the conditions were approximated.[8] In order to settle this point two things were done, (1) the temperature of a point near the surface of the specimen was tested by means of a thermojunction placed there and (2) these tests were made at different rates of water flow. The first tests showed that within the uncertainty of the effective distance of the junction from the surface of the specimen, a point which could be considered to be within a few thousandths of a centimeter from the surface came up to the water temperature as rapidly as can be predicted from the theory based upon an instantaneous temperature change at the surface. The second tests showed no significant difference in the results.

Slight changes in the water temperature itself during a run have no serious effect if they occur shortly after the initial impulse. Each successive impulse will after a moderate interval reduce to substantially a single exponential and therefore the sum also will reduce to a single exponential. Changes which occur later in the run do produce an error however, which probably is the chief error remaining in the apparatus and accounts for the major part of the difference between results of different runs. In several runs changes of about 0.01°C were observed and an approximate correction applied.

The thermojunctions in the specimen may be several thousandths of a centimeter from the positions on which calculations are based, but this is of no consequence, since the small third harmonic thus introduced would disappear long before the time at which observations are utilized.

The thermocouple leads are passed under a block of metal shortly after being brought out of the apparatus in order that the change in temperature of the galvanometer circuit may be limited to a short portion near the specimen. Thus the change in resistance of the galvanometer circuit during a run is kept within about 0.03 percent.

The electrical time constant of the galvanometer circuit is of the order of 10^{-4} second or less and hence can be ignored. The quantities m and n compare with p as below:

$$m = 0.63;\ n = 4.0;\ p = 0.0041.$$

[8] A calculation of the thermal resistance of the so-called "film" of water which might be conceived to exist at the top of the specimen can give such magnitude as to be quite appreciable or entirely insignificant, depending upon the assumptions made and the heat-transfer data selected. These data vary quite widely, and to the writer's knowledge there are none which relate at all closely to the conditions of this experiment. In this experiment the liquid impinged with a jet action directly upon a small surface from which the heat was transferred, causing a condition of extreme turbulence, and the quantity of water used was very great in proportion to the heat removed (about 10,000 gm per cal). Most heat-transfer data are average figures computed for flow parallel to the walls of relatively long pipes through which considerable heat is transferred.

The precise calculation of M and N is quite tedious, but it can be shown very readily by means of a rough calculation that they are sufficiently small that the terms $M\epsilon^{-mt}$ and $N\epsilon^{-nt}$ vanish within much less than 60 seconds.

The results obtained thus far represent an average over about a 5°C range in the neighborhood of 25°C, and since the diffusivity varies about 0.1 percent per degree C the exact temperature for which the results apply cannot be stated. This however is not a serious flaw in the method, since by introducing higher galvanometer sensitivity and better temperature control, the temperature interval can be much reduced. In fact, by the expenditure of more money for more elaborate apparatus, the expenditure of more time and effort, and the use of several observers, the writer believes that the precision of the determination could be improved far beyond that attained in the following example.

IV. Specific Example

The following are the results of a series of runs on a nickel specimen of the following analysis.[9]

Cobalt	0.01 percent	Manganese	0.23 percent
Copper	0.06	**Nickel**	**99.23**
Carbon	0.12	Silicon	0.06
Iron	0.27	Sulphur	0.07

The specimen is cold drawn rod obtained from H. Boker and Company, Inc., ground to precise diameter by courtesy of Cincinnati Grinders Incorporated.

Six runs gave the following results, uncorrected for the pendulum calibration:

Run	p	ΔT	Average T
11	$0.004,103,8 \pm 0.000,001,1 \text{sec.}_{-1}$	5.64°C	25.16°C
13	$0.004,093,6 \pm 0.000,001,1$	4.80	24.70
14	$0.004,104,0 \pm 0.000,002,2$	4.92	24.55
15	$0.004,086,8 \pm 0.000,001,5$	5.27	24.84
16	$0.004,097,5 \pm 0.000,001,0$	4.86	24.64
17	$0.004,076,1 \pm 0.000,002,0$	5.29	24.80

From these runs the most probable value is,

$$p = 0.004,093,6 \pm 0.000,003,1 \text{sec.}_{-1}.$$

The reason for the probable error of the final result being larger than the probable error for the individual runs is believed to be due almost entirely to slight changes in water temperature during the runs.

[9] Analysis by Arthur D. Little, Inc.

From the pendulum calibration a correction factor of 1.00063 ± 0.00005 must be applied, giving finally,

$$p = 0.004,096,2 \pm 0.000,003,1 \text{ sec.}_{-1}$$

But

$$p = \frac{k\pi^2}{4c\rho L^2},$$

$$L = 9.501 \pm 0.001 \text{ cm} \quad \text{and}$$

$$\rho = 8.848 \pm 0.004 \text{ gm cm}^{-3}.$$

Hence

$$\alpha^2 = 0.14985 \pm 0.00012 \text{ cm}^2 \text{ sec.}_{-1}$$

and

$$\frac{k}{c} = 1.3269 \pm 0.0012 \text{ gm cm}^{-1} \text{ sec.}_{-1}$$

V. Acknowledgment

The writer is particularly indebted to Dr. V. Bush for encouragement and guidance in this work, and wishes to express appreciation also for the interest and suggestions from numerous other colleagues with whom the work was discussed.

A SLOWLY CONTRACTING OR EXPANDING FLUID SPHERE AND ITS STABILITY

By Herman Roth
Mendenhall Laboratory of Physics, Ohio State University

(Received December 9, 1931)

Abstract

It has been pointed out by Thomas that, if a solution of the equations of equilibrium for a slowly contracting or expanding fluid sphere has been obtained, the exact conditions of dynamical stability can be applied without difficulty. A particular solution of the equations of radiative equilibrium for a fluid sphere contracting homologously without internal generation of energy has been obtained. The opacity was assumed to obey Kramers formula. By assuming a central temperature and total pressure of the order of magnitude expected for stellar interiors, the logarithmic rate of contraction was adjusted so that the boundary conditions, *viz.*, $P=0$, $T=0$, for a finite r and m, were satisfied. This solution has been found to be dynamically stable (at least for radial displacements) for values of the ratios of specific heats of material between 5/3 and 1 corresponding to all possible values of the specific heat at constant volume of a perfect gas.

Introduction

PREVIOUS investigations* of the stability of stellar models have usually been made by considering a varied motion constrained to have one or two degrees of freedom, e.g., a uniform dilatation. If the constrained motion is unstable, the model is unstable; while if the constrained motion is stable, the model may or may not be stable. Thomas[1] has pointed out that if a solution of the equilibrium equations for a slowly contracting or expanding fluid sphere has been obtained, the complete conditions for dynamical stability can be applied readily.

With this in view, a solution was obtained of the equilibrium equations for a fluid sphere, which contracts or expands homologously without internal generation of energy, and for which the opacity is given by Kramers[2] formula. The conditions for dynamical stability were then applied and this model was found to be dynamically stable.

Part I. Solution of Equations

The equations of equilibrium for a fluid sphere in radiative equilibrium contracting homologously without internal generation of energy are:

$$\frac{dP}{dr} = -\frac{\rho G m}{r} \tag{1.1}$$

$$\frac{L}{4\pi r^2} = \frac{c}{3k\rho}\frac{d}{dr}(aT^4) \tag{1.2}$$

* Jeans, reference 2, p. 118. H. Vogt, Jena Observatory Bulletin **2**, 10 (1929).
[1] L. H. Thomas, Monthly Notices of the Royal Astronomical Society **XCI**, 624 (1931).
[2] Jeans, Astronomy and Cosmogony, 1929, p. 84.

$$(3R - C_v)\rho T \frac{f'}{f} = \frac{1}{4\pi r^2} \frac{dL}{dr} \tag{1.3}$$[3]

where

$$\frac{dm}{dr} = 4\pi r^2 \rho \tag{2.1}$$

$$P = p + p_r = \rho RT + \tfrac{1}{3} aT^4 \tag{2.2}$$

The notation is that of Eddington.[4] P is the total pressure, p_r the radiation pressure, p the gas pressure, T the temperature, ρ the density, L the luminosity, at a radius r, f'/f the logarithmic rate of contraction, and m the mass contained within a radius r. c is the velocity of light, a is Stefan's constant, R is the universal gas constant, G the constant of gravitation, and C_v the specific heat of a gas at constant volume. We take the opacity k as given by Kramers' formula;[5]

$$k = 4.46 \times 10^{25} Z^2/A\mu \cdot \rho T^{-3.5}$$

with $Z^2/A\mu = 12.5$. By putting in the values of the physical constants, and by using convenient units, viz.:

P, 10^{12} dynes/cm^2; T, 10^6 degrees absolute; m, 10^{33} grams; r, 10^{11} cm; L, 10^{35} ergs/cm^2; we find:

$$\frac{dT}{dm} = -2.793 \times 10^5 \frac{Lp}{r^4 T^{7.5}} \tag{4.1}$$

$$\frac{dp}{dm} = -53.00 \frac{m}{r^4} - 1.019 \times 10^{-2} T^3 \frac{dT}{dm} \tag{4.2}$$

$$\frac{dr}{dm} = 3.287 T/r^2 p \tag{4.3}$$

$$\frac{dL}{dm} = \alpha T \tag{4.4}$$

where P has been replaced by $p + 1/3 aT^4$ and

$$\alpha = 0.6195 \times 10^{12} f'/f$$

for

$$C_v = 3/2\, R.$$

It is to be noted that a change in C_v will alter α but will not change its order of magnitude, unless $C_v \approx 3R$ when the contraction or expansion becomes very rapid and our equations break down.

With central temperature and total pressure equal to 5×10^6 degrees absolute and 8.5917×10^{12} dynes per cm.^{2} (gas pressure 7×10^{12}) respectively, we computed two solutions corresponding $\alpha = 0.17$ and 0.175. ($f'/f = 2.74 \times 10^{-13}$,

[3] L. H. Thomas, M.N.R.A.S. **XCI,** 122 (1931).

[4] Eddington, Internal Constitution of the Stars, 1929.

[5] Jeans, reference 2, p. 84.

or a past life of 10^5 years). In the first of these solutions, the pressure approached zero and the temperature remained finite and in the second, the termperature approached zero and the pressure remained finite as m increased. By interpolating between these two solutions,[6] a solution for which both became zero within one mass interval was found. These solutions are given in Table I.

TABLE I. *Solutions of equations.*

	$\alpha=0.17$				$\alpha=0.175$			
$M\times10^{-33}$	$P\times10^{-12}$	$T\times10^{-6}$	$r\times10^{-11}$	$L\times10^{-35}$	$P\times10^{-12}$	$T\times10^{-6}$	$r\times10^{-11}$	$L\times10^{-35}$
0	7	5	0	0	7	5	0	0
0.1	5.6196	4.7783	0.89570	0.085	5.6196	4.7718	0.89570	0.0875
0.15	5.1976	4.6949	1.0699	0.12562	5.2010	4.6852	1.0696	0.12926
0.2250	4.7298	4.5591	1.2645	0.18548	4.7366	4.5848	1.2638	0.19076
0.270	4.5448	4.5529	1.3545	0.22066	4.5532	4.5360	1.3536	0.22680
0.324	4.3422	4.5009	1.4515	0.26246	4.3524	4.4804	1.4500	0.26966
0.3588	4.1208	4.4423	1.5563	0.31204	4.1330	4.4178	1.5542	0.32046
0.4666	3.8794	4.3761	1.6701	0.37080	3.8930	4.3462	1.6680	0.38060
0.5600	3.6170	4.3011	1.7943	0.44028	3.6322	4.2642	1.7914	0.45164
0.672	3.3334	5.2159	1.9303	0.52218	3.3516	4.1698	1.9260	0.53522
0.8064	3.0280	4.1191	2.0797	0.61850	3.0498	4.0604	2.0742	0.63330
0.9676	2.7016	4.0087	2.2463	0.73138	2.7278	3.9322	2.2382	0.74784
1.1604	2.3570	3.8833	2.4327	0.86276	2.3886	3.7804	2.4206	0.88052
1.391	1.9968	3.7407	2.6437	1.0150	2.0358	3.5964	2.6254	1.0331
1.669	1.6220	3.5783	2.8887	1.1918	1.6718	3.3634	2.8596	1.2081
2.003	1.2404	3.3961	3.1789	1.3950	1.3082	3.0478	3.1298	1.4047
2.403	0.8616	3.1989	3.5351	1.6260	0.96600	2.5462	3.4426	1.6181
2.883	0.49696	3.0027	4.0039	1.8870	0.71400	1.1984	3.7936	1.8319
3.459	0.16286	2.8481	4.7175	2.1810				
		Interpolated Solution $\alpha=.17$						
1.1604	2.3700	3.8300	2.4300	0.88052				
1.391	2.0156	3.6680	2.6386	1.0306				
1.669	1.6430	3.4842	2.8774	1.2040				
2.003	1.2688	3.2532	3.1586	1.4018				
2.403	0.92020	2.9662	3.4964	1.6230				
2.883	0.57260	2.5812	3.9124	1.8650				
3.459	0.26420	1.9834	4.4699	2.1178				
4.151	0.04140	0.3880	5.3245	2.3512				

A solution for which p tends to zero while T remains finite has no physical meaning because it approaches an isothermal solution at large distances and thus has infinite mass. The other solution for which T tends to zero and p remains finite, has a finite mass. As the surface is approached, the above equations of equilibrium break down as soon as the outward flow of radiation is comparable to the total radiation present. We believe that it is possible to fit an atmosphere in *adiabatic* equilibrium to such an interior, provided that the pressure remaining is not too large.

All the solutions for stars of this mass contracting homologously can be obtained by altering the internal pressure, temperature, and radius, for a given included mass in proportions given by Lane's law, *viz.*:

$$T \propto r^{-1} \quad p \propto r^{-4}.$$

[6] Eddington, Internal Constitution of the Stars, p. 125.

Further:

$$L \propto r^{-1/2}$$

$$l \propto r^{-1/2}$$

$$T_e \propto r^{-5/8}$$

where l is the past life, and T_e is the effective temperature.

The mass of this star is about that of β Aurigae A or of Sirius A.[7] The luminosity per gram corresponding to the radius of Sirius would be 1.9 times that of the Sun. As in Eddington's model, the luminosity is too small.

Part II. Dynamical Stability

Besides the condition of dynamical equilibrium, there are three conditions of stability—the Euler, the Legendre, and the Jacobi. The first two of these relate to the matter at each point in the solution while the last relates to the solution as a whole. If the matter at each point is stable by itself, the first two hold. The Jacobi condition demands that for any adiabatic displacement of the solution there shall be no point m in the solution for which the value of r remains unchanged. The last condition is applied to this solution below.

The entropy of a perfect gas with radiation is given by:

$$s = 4/3\, aT^3\sigma + \int C_v/T \cdot dT + R \log \sigma.$$

The total pressure is given by:

$$P = \tfrac{1}{3}aT^4 + RT/\sigma$$

where $\sigma = 1/\rho$ = volume per unit mass.

By taking $\delta s = 0$, we derive:

$$\delta\sigma = -\frac{\delta P}{RT/\sigma^2 + \dfrac{(4/3\, aT^3 + R/\sigma)^2}{(4aT^2\sigma + C_v/T)}}.$$

Then, with (1.1) and (2.1), we obtain

$$\frac{d}{dm}(\delta P) = \frac{Gm\delta v}{4\pi r^7}$$

$$\frac{d}{dm}(\delta v) = -\frac{\sigma\delta P}{P\gamma}$$

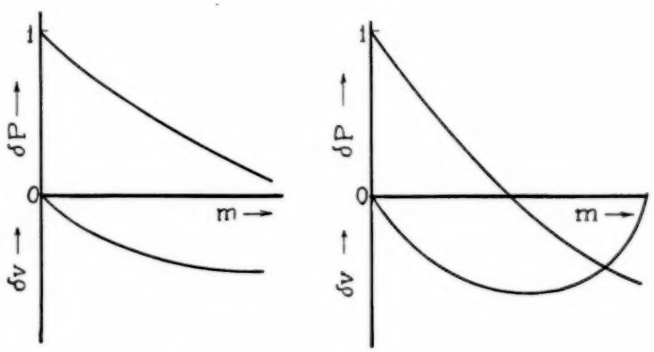
where $v = 4/3\pi r^3$
and

$$\gamma = \frac{\sigma}{P}\left[\frac{RT}{\sigma^2} + \frac{(4/3\, aT^3 + R/\sigma)^2}{4aT^2\sigma + C_v/T}\right]$$

This is the same γ as given by Eddington.[8]

[7] Jeans, reference 2, p. 59.
[8] Eddington, reference 4, p. 191.

Starting with $\delta P = 1$ and $\delta v = 0$ for $m = 0$, δv was computed at each point in the solution of the equilibrium equations. The Jacobi condition demands that there is no other point for which δv is zero, ($\delta v = 4\pi r^2 \delta r$). The diagrams show how δP and δv vary with m for stable (I) and unstable (II) solutions.



Figs. 1 and 2. Stability curves.

For $C_v = 3R/2, \gamma = 5/3$ the test was applied exactly. For the limiting cases $C_v = 3R$, $\gamma = 4/3$, and $C_v = \infty$, $\gamma = 1$; γ is constant throughout the star; but in the former case, our tests are only approximate on account of the rapid contraction or expansion.

We obtain curves such as I and conclude that the star is dynamically stable in all these cases.

I wish to thank Dr. L. H. Thomas for the suggestion of this problem and for considerable assistance during its progress.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

On the Electric and Photoelectric Properties of Contacts between a Metal and a Semiconductor

In a previous paper one of us has developed a theory of the electric resistance of contacts between two metals, based upon the idea that a contact can be treated as a gap of a definite width much larger than the atomic distance, through which electrons penetrate according to the laws of wave mechanics.[1]

The dependence of the current strength I upon the potential difference across the gap V_1 is determined for very small values of V_1 by Eq. (7) loc. cit. For larger values of V_1 the Fermi distribution function $f_a(W_x+R)$ where $R=W_y+W_z$ cannot be replaced by $f_b(W_x+U_{ab}+R)$ so that we get the following exact formula

$$I=\frac{2\pi}{m^2}\int_0^\infty dW_x D_1(W_x)\int_0^\infty dR[f_a(W_x+R)-f_b(W_x+R+U_{ab}+V_1)]. \tag{1}$$

$D_1(W_x)$ is the transmission coefficient through the contact for electrons which in a have kinetic energy W_x in the x-direction.

The letter a refers as before to that metal for which $W_a<W_b$, i.e., which is the poorer conductor, or to the semiconductor, b denoting the good metal. $W^b=W_x+R+U_{ab}+V_1$ is the kinetic energy in b of an electron which has a kinetic energy W_x+R in a (the total energy being the same in both cases). Only such electrons will be able to pass from b to a for which $W_x{}^b>U_{ab}+V_1$. The equilibrium equation $f_a(W_x)=f_b(W_x+U_{ab})$ is valid accordingly for $W_x{}^b>U_{ab}$ only. For smaller values of $W_x{}^b$, $f_b(W_x{}^b)$ cannot be replaced by $f_a(W_x{}^b-U_{ab})$ as was done in the previous paper.

A semiconductor can be treated in exactly the same way as a metal with a relatively small number of free electrons n_a per unit volume. Putting $n_a=\iiint_{-\infty}^{+\infty} f_a dr_x dr_y dr_z$ and $f_a=2(m/h)^3 e^{(W-W_a)/kT}$ according to Maxwell's law, to which Fermi's law reduces for small values of n_a, we get

$$W_a=kT\log\frac{n_a h^3}{2(2\pi mkT)^{3/2}},$$

where n_a as a function of the temperature T is given by the equation

$$n_a=N_a e^{-\epsilon_a/kT}.$$

With $n_a=10^{12}$, 10^{15} and 10^{18}, we get for W_a *negative* values $W_a=-18kT$, $-11kT$, $-9.5kT$ respectively. The corresponding quantity for the metal b (W_b) is positive and approximately equal to the maximum kinetic energy of the electrons at $T=0$. Putting $f_b=2(m/h)^3(1/(e^{(W-W_b)/kT}+1))$ we get from (1)

$$I=\frac{4\pi kTm}{h^3}\int_0^\infty dW_x D_1(W_x)[e^{-\alpha(W_x-W_a)}-\log(1+e^{-\alpha(W_x-W_a+V_1)})] \tag{2}$$

where $\alpha=1/(kT)$. In the case of a sufficiently large positive value of V_1 (electrons flowing from a to b) we can put

$$\log(1+e^{-\alpha(W_x-W_a+V_1)})\cong e^{-\alpha(W_x-W_a+V_1)},$$

whence

$$I=I_0(1-e^{-\alpha V_1}) \tag{3}$$

with

$$I_0=\frac{n_a}{(2\pi mkT)^{1/2}}\int_0^\infty dW_x D_1(W_x)e^{-\alpha W_x}$$

denoting the "saturation" value of the current in the direction ab. For the opposite direction we get in the same way, *so long as* $|V_1|$ *is smaller* than $|W_a|=-W_a$

$$I=I_0(e^{\alpha|V_1|}-1). \tag{3a}$$

These equations express a very high rectification effect in the direction metal semicon-

[1] J. Frenkel, Phys. Rev. **36**, 1604 (1930).

ductors, the relative abundance of electrons in the former becoming effective for such values of V_1 which are larger than kT and smaller than $-W_a$.[2] Putting $D_1(W_x) = e^{-\gamma(U_a - W_x^{1/2})}$, we have approximately

$$I_0 = n_a\left(\frac{kT}{2\pi m}\right)^{1/2} \frac{e^{-\gamma(U_a)^{1/2}}}{1 - \dfrac{\gamma kT}{2(u_a)^{1/2}}}$$

or since $n_a = N_a e^{-\epsilon_a/kT}$

$$I_0 = A(T)^{1/2} e^{-\epsilon_a/kT}. \qquad (3b)$$

This expression for the "saturation" current is similar to that which corresponds to the Richardson effect.

As a matter of fact D_1 increases with increase of the applied p.d. V_1 according to the equation

$$D_1 = D_0 e^{\beta|V_1|}$$

with $\beta \leqq 1.5$ if V_1 is expressed in volts, which explains the actual lack of saturation, since I_0 in (3) and (3a) is replaced by the product of (3b) with $e^{\beta|V_1|}$. If $-V_1 = |V_1|$ is larger than $-W_a = |W_a|$ we can replace $\log\left[1 + e^{-\alpha(W_x - W_a + V_1)}\right]$ by $\alpha(|V_1| - |W_a| - W_x)$ so long as $W_x < |V_1| - |W_a|$ and neglect it altogether in the opposite case. This gives by (2) for the current in the direction *ba*:

$$|I| = \left[\frac{2\pi m}{h^3}(|V_1| - |W_a|)^2 e^{-\gamma(U_a)^{1/2}} - I_0\right] e^{\beta|V_1|} \qquad (4)$$

The first term in the square brackets is practically independent of the temperature while the second rapidly increases with it (according to (3b)). This seems to explain the disappearance of rectification for sufficiently high temperatures.

The illumination of the place of contact between a metal and a semiconductor, Cu and Cu_2O say, produces, as has been first shown by Lange, an unusual photoelectric effect, which consists in the flow of electrons from Cu_2O (a) into Cu (b). This "contact" photoelectric effect is intimately connected with the "inner" photoelectric effect of Cu_2O, revealed by the increase of its conductivity under illumination. The low value of the threshold frequency for the contact effect (0.7 volt) compared with the outer one (~4 volts) is due to the fact that the electrons can pass through the potential energy mountain across the gap with negative kinetic energy. The fact that it is somewhat higher than for the inner effect is probably due to the increase of the transparence coefficient $D(W_x)$ with increase of the initial kinetic energy of the electrons set free by the light. The fact that the latter does not produce a current from the metal into the semiconductor, is due to the relatively small probability of the photoelectric effect for a "free" electron (in the metal) compared with the probability of this effect for a "bound" electron (in the semiconductor). The current I_0 directly produced by the light can be assumed to be practically independent of the temperature. Now the stream of electrons coming from the semiconductor into the metal will cause a change of the contact p.d. between them by a certain amount V_1, which in its turn will produce a current in the reverse direction. If there is no other connection between the two bodies, V_1 will reach a stationary value defined by the equality of the two currents, i.e. by the equation

$$I_c = I_0(e^{V_1/kT} - 1),$$

or so long as the photoelectric potential difference V_1 is small compared with kT (as a matter of fact it is of the order of magnitude of a few millivolts, i.e., about 10 times smaller than kT)

$$V_1 = \frac{kT}{I_0} \cdot I_c.$$

This formula explains the dependence of V_1 on the intensity of light (as measured by I_c) the temperature (I_0 rapidly increases with T) and upon the transmission coefficient D to which I_0 is proportional. In the case of a good contact the photoelectric e.m. force V_1 will be vanishingly small—just as well as the rectification, which requires sufficiently large values of V_1 obtainable only with relatively poor contacts (i.e., small values of I_0). For a detailed treatment of the subject outlined in this note the reader is referred to the first issue of the "Physics of the Soviet Union"—a new Russian journal in foreign languages which will be issued monthly from the end of January 1932.

J. Frenkel
A. Joffé
Leningrad, Physico-Technical Institute,
November, 1931.

[2] It should be remembered that V_1 denotes that part of the *e.m.* force acting in the circuit which corresponds to the contact gap alone. *A relatively high resistance of the contact is thus essential for the rectification action.* Expressions of exactly the same type as (3) and (3a) have been recently obtained by C. Wagner (Phys. Zeits. **32,** 584, 1931) with the help of an entirely different picture of the mechanism of rectification which we think to be highly improbable.

On a General Method of Treating Uncomplete Systems in Quantum Mechanics

Let us divide the variables specifying a complicated system into two sets x and q. The corresponding Hamiltonian H can be divided accordingly into three parts, K depending upon x alone (and the associated operators $(h/2\pi i)(\partial/\partial x)$), L depending on q alone, and U depending both upon x and q. U can be considered as the mutual energy of those two parts of the system A and B which are specified by the variables x and q.

Denoting the characteristic values and functions of L with L' and $x_{L'}$ we can expand the solution of $(H-H')\psi_{H'}=0$ into a series

$$\psi = \sum_{L'} \phi_{L'}(x) x_{L'}(q) \tag{1}$$

where the functions $\phi_{L'}(x)$ which play the role of expansion coefficients can be easily shown to satisfy the equation

$$K\phi_{L'} + \sum_{L''} U_{L'L''}\phi_{L''} = (H' - L')\phi_{L'} \tag{2}$$

with

$$U_{L'L''} = \int x^*_{L'} U x_{L''} dq.$$

Eq. (2) can be written in the matrix form

$$J\phi = J' \cdot \phi \tag{3}$$

if ϕ is defined as a one-column matrix with the elements $\phi_{L'}$ and J as a two-dimensional operator matrix with the elements

$$J_{L'L''} = K\delta_{L'L''} + U_{L'L''}. \tag{4}$$

It can be regarded as a sort of generalization of Pauli's or Dirac's equation for the spinning electron, the characteristic values of L playing the role of the spin coordinates. If the system under consideration is a complicated particle which we wish to treat as a material point moving in an external field of force, then we can define x as the coordinates of the center of gravity and replace the coordinates q specifying the inner motion by the corresponding quantum numbers L'. The properties of the particle (atom, molecule) due to its inner motion will be represented by matrices, which may be considered as a generalization of Pauli's or Dirac's spin matrices (we have for example in the case of the motion of an atom in an electric field $E(x)$: $U_{L'L''} = -E(x) \cdot P_{L'L''}$, where $P_{L'L''}$ are the matrix elements of the electric moment of the particle). The same method can be applied to the interaction between two particles, treated as material points, as this has been done by Fermi[1] in his theory of the hyperfine structure of the spectra. The nucleus is specified here by a matrix representing its magnetic moment and its mutual action with the electron is treated as a one-sided perturbation due to the magnetic field of the nucleus (considered as an external field).

A similar replacement of the mutual action of two parts of a system A and B by a one-sided action of one of them B on the other A is found in Heisenberg's theory[2] of the interaction between matter A and radiation B. In this theory the uncomplete Hamiltonian $K+U$ is used to specify the system, without the part L appearing in Dirac's theory, the results of both theories being the same so long as U is treated as a matrix with regard to the quantized states of the e.m. field.

Neither Fermi nor Heisenberg seem to have recognized the general character of the method which they have used and the possibility of establishing its strict validity as has been shown in this note.

J. Frenkel
Leningrad, Physico-Technical Institute,
November, 1931.

[1] Fermi, Zeits. f. Physik **60**, 320 (1930).
[2] Heisenberg, Ann. d. Physik **9**, 338 (1931).

Quantitative Study of the Quenching of Fluorescence and of the Transfer of Energy in Iodine Vapor

As it has already been shown by Wood, the resonance spectrum of iodine undergoes two types of change when its vapor pressure is increased or a foreign gas is mixed with it. We have first the total weakening of the spectrum, due to the dissociation of the excited molecules upon collision with normal ones, (quenching). The second effect is the appearance of a new spectral series of iodine, corresponding to transitions from other vibrational levels of the excited molecule to those of the normal one. Thus a collision of an excited molecule (J'_2) with another one (u) leads to two processes:

$$J'_2 + u \rightarrow J + J + u \text{ (quenching)}, \tag{1}$$

$$J(v'_1) + u \rightarrow J_2'(v'_2) + u \text{ (transfer of energy)}. \tag{2}$$

This investigation was undertaken in order to establish some quantitative relations between the probabilities of both processes. Hydrogen and nitrogen were used as foreign gases.

The resonance series excited by the green and yellow lines of mercury were studied. The results are as follows:

In the hydrogen mixture, in the case of the excitation by the line 5461A we have transitions

$$v' = 26 \rightarrow 25, 24 \text{ and } 27, 28.$$

The collision radius corresponding to the change of the vibrational energy to one quantum ($\Delta v' = \pm 1$) is approximately 4 times greater than the gas-kinetic one, while in the nitrogen mixture correspondingly 12 times greater than the gas-kinetic one. In the nitrogen mixture, beside the above process ($v' = 26 \rightarrow 25, 24, 27, 28$) a considerable change of the rotational energy is taking place—in agreement with Oldenberg's considerations. The effect is manifested in the appearance of a continuous background of considerable intensity, while in the hydrogen mixtures it is practically absent.

All the members of a certain series are reduced in intensity quite equally. The same results were obtained by Turner in his experiments with the quenching of iodine fluorescence by magnetic field. In contradiction with Turner's results we have found that within the experimental error (20 percent) the resonance series excited by different lines are weakened equally.

Full details of this investigation are going to be published shortly in the new Journal of Physics of U.S.S.R.

M. ELIASHEVICH
Chemical-Physical Institute, Leningrad,
December 14, 1931.

The Ultraviolet Absorption Spectrum of Ozone

We have investigated the ultraviolet absorption of ozone as it is formed in an ozonator in the moment of a silent current passing through it. In the range of frequencies 29000–33000 cm^{-1} 75 bands were measured with an accuracy of about 5 cm^{-1} for most of them. The band-heads may be represented with sufficient accuracy by the following formula:

$$\nu = 29404 + 335,5(v'_1 + \tfrac{1}{2}) - 7,5(v'_1 + \tfrac{1}{2})^2 + 59(v'_2 + \tfrac{1}{2}) - 433(v''_1 + \tfrac{1}{2}).$$

Our frequency 433 cm^{-1} practically coincides with that of 435 cm^{-1} obtained by Wulf (Proc. Nat. Acad. Sci. **16,** 507, 1930) from the analysis of the visible spectrum of ozone. This frequency, as it seems, must be interpreted as due to the transverse vibrations ν_1 (Mecke's deformational vibrations) of the molecule O_3SO that a linear form must be assigned to it. In that case according to Dennison, the following relation must exist between the two longitudinal frequencies $\nu_3 : \nu_2 = (3)^{1/2}$, ν_2 being optically inactive.

From the infrared spectrum of ozone we have $\nu_3 = 1015$ cm^{-1}. The above relation gives $\nu_2 \sim 590$ cm^{-1}. Assuming that the asymmetry of the absorption band of O_3 at 9.85 (1015 cm^{-1}) is due to its overlapping with the band $\nu_2 + \nu_1$, we obtain $\nu_2 \sim 670$ cm^{-1}.

In the range of frequencies 33000–42000 cm^{-1} we have found, in agreement with Wulf and Melvin (Phys. Rev. **38,** 330, 1931) a set of series, consisting of diffuse bands with the frequency separation of 0.300 cm^{-1} in each case.

A detailed description and discussion of this investigation will soon appear in the new Journal of Physics of U.S.S.R.

A. JAKOWLEVA
V. KONDRATJEW
Chemical-Physical Institute, Leningrad,
December 14, 1931.

On the Entropy of the Universe

Tolman in his paper "On the Problem of the Entropy of the Universe as a Whole" (Phys. Rev. **37,** 1639, 1931) advances a suggestion, page 1642, which he attributes to some remarks of the late Professor William James about which he learned in conversation with Professor Gilbert N. Lewis. It is, "to assume an infinite past for the universe, coupled with ever decreasing values for the entropy of the universe as we examine backwards in the past and a continuous asymptotic approach to the maximum of entropy in the future". Doubtless Professor Tolman did not know of my article of 1911 (Il Nuovo Cimento **57,** 85, 1911) "Circa una maggiore precisazione della legge di degradazione dell energia e circa una possibile disponibilita indefinita di energia degradabile". The priority for the above suggestion therefore belongs exclusively to me. The hypothesis is just as valid for an infinite

universe as for a finite since it is the ratio of all the entropy of the universe to all the matter of the universe which is considered and this ratio is finite.

The hypothesis of a universe of infinite extent was advanced for the first time (about 1600) by the Italian philosopher Phillipe Brun (called Jordan Bruno) in his book "De L'infinito, Universo e Mondi".

PASQUALE BARRECA

Reggio en Calabre, Italy,
December 14, 1931.

Molecular Configuration of N_2O

We should like to congratulate Professor Barker and Dr. Plyler on the beautiful experimental work described in "The Infrared Spectrum and the Molecular Configuration of N_2O" (Phys. Rev. **38,** 1827 (1931)). At the same time we feel we must comment upon the deductions made as to the molecular structure of nitrous oxide, which they suggest is N $\equiv$ N $=$ 0. The force constants representing the bindings between the two nitrogen atoms and between the central nitrogen and the oxygen atom are stated to be $K_1 = 24 \times 10^5$, and $K_2 = 22 \times 10^5$ dynes per cm respectively. If these have been correctly evaluated, the formula of the substance should be N $\equiv$ N $\equiv$ 0, since such values correspond to triple linkings (see, for example, Bailey and Cassie, Proc. Roy. Soc. **A132,** 247 (1931)).

In a paper now in the course of publication in the Proceedings of the Royal Society, and dealing with the absorption spectrum of carbonyl sulphide, we have calculated the fundamental nodes of vibration for the asymmetrical rectilinear molecule: the relation between the masses, the force constants, and the frequencies will be found to be given by

$$p_1^2 + p_2^2 = K_1(1/m_1 + 1/m_2) + K_2(1/m_2 + 1/m_3),$$
$$\text{and } p_1^2 p_2^2 = (1/m_1m_2 + 1/m_2m_3 + 1/m_3m_1)K_1K_2,$$

where $p = 2\pi\nu c$. On substituting the frequencies corresponding to the two longitudinal vibrations, 1285 and 2224 cm^{-1}, it will be seen that $K_1 + K_2 = 26.8 \times 10^5$ dynes per cm and $K_1K_2 = 197 \times 10^{10}$. The consistent solution is $K_1 = K_2 \backsimeq 14 \times 10^5$ dynes per cm. These values correspond to double bonds in each case, the formula being N $=$ N $=$ 0, or :N̈::N::Ö:. constructed from N^-N^+O.

C. R. BAILEY
A. B. D. CASSIE

Department of Chemistry,
University College,
London, England,
January 4, 1932.

Evidence on the Ionization Potentials of O_2

In a certain commercial process, an oxide surface is transformed by means of an intermittent discharge in one of the noble gases, the oxide surface being one electrode. In a study of this process, it was noticed that the transformation proceeded rapidly in very pure argon, less rapidly in very pure helium, and not at all in very pure neon. The addition of a few hundredths of a percent of argon to the neon, however, caused the transformation to proceed rapidly.

This immediately recalls the work of Penning[1] on the great effect of extremely small amounts of some impurity whose molecules could be ionized by neon metastables, for example, on the sparking potential in neon, and suggests that this process plays some part in the intermittent transforming discharge. In the case of argon or helium some other gas must play the role played by argon in neon. Of the three possible impurities, carbon monoxide, hydrogen, and oxygen (from the oxide surface), the known ionization potentials of the two former gases are too high to permit ionization by argon metastables. Smyth[2] gives 13(?) volts for the I.P. of O_2 from electron impact data, but Mulliken[3] has computed 11.7 volts from band spectra. This latter value agrees very closely with the energy of the argon metastable level (11.68 volts). The second ionization potential of O_2 lies 7.5 volts above the first,[2] or, with Mulliken's value, at 19.2 volts, sufficiently near the helium metastable level at 19.8 volts to make ionizing interaction likely. Conversely, if we assume that these ionizing interactions are the explanation of the observations, Mulliken's value of the I.P. is supported.

[1] F. M. Penning, Zeits. f. Physik **57,** 723 (1929).

[2] H. D. Smyth, Rev. Mod. Phys. **3,** 389 (1931).

[3] R. S. Mulliken, Phys. Rev. **37,** 1711 (A) (1931).

I am indebted to Mr. T. E. Foulke and Mr. T. J. Radcliffe of the General Electric Vapor Lamp Company, in whose laboratory these observations were made, for observational data.

EUGENE W. PIKE
At present Greifswald/Pom.
Stralsunderstrasse 16¹,
Germany,
January 6, 1932.

Raman Effect in Water Vapor

With the use of a high speed glass spectrograph and a very intense light source we have been successful in obtaining the Raman spectrum of water vapor excited by the total radiation of the mercury arc in the visible and near ultraviolet regions of the spectrum. The water vapor was sealed in a Pyrex tube and was at a temperature of about 275°C and at a pressure of between two and three atmospheres.

The observed Raman lines correspond to shifts of 3654 (± 5) cm^{-1}, 1648 (± 5) cm^{-1}, and 984 (± 10) cm^{-1}. On the basis of the selection rules which apply in Raman spectra[1] these are interpreted as pure vibration frequencies and represent the three fundamentals to be expected for the water molecule. The two longer shifts correspond to infrared frequencies of 2.73μ and 6.06μ, respectively, and must be the counterparts of the strong absorption bands near 2.66μ and 6.26μ which were first classed as fundamentals by Hettner.[2] The third shift corresponds to infrared absorption at 10.16μ which is very nearly inactive in ordinary absorption or emission spectra although some weak absorption does show in this region. This shift is probably to be correlated with Dennison's[3] ν_1 which would be nearly inactive for suitable force constants within the molecule. The 3654 cm^{-1} shift probably corresponds to Dennison's ν_3 since the latter motion would closely approach that of mutual vibration of an hydrogen atom with an oxygen atom and since this frequency so nearly corresponds to the vibration of the normal OH molecule, 3568 cm^{-1}. Mecke[4] has previously attributed the 2.7μ fundamental to the OH band. The 1648 cm^{-1} frequency must then represent Dennison's ν_2.

Our observations of the 3654 cm^{-1} shift confirm the work of Daure and Kastler[5] who reported a Raman frequency of 3655 (± 5) cm^{-1} in an exposure of 50 to 70 hours duration. On one of our clearest plates this frequency shift made its appearance in a 16 hour exposure, scattered from the exciting lines λ3650 and λ3655. Considerably longer exposures showed scattering of the same frequency from λ3663 and from λ4047.

Evidence for the 1648 cm^{-1} vibration frequency rests on Raman scattering to the long wave-length side of λ3650, λ3655 and λ4047 and the further appearance of two lines close to positions calculated for anti-Stokes lines from λ4047 and λ4358. The frequency shifts computed from all of the Raman lines are in good agreement. The scattering from λ3650 and λ3655 was particularly intense and showed clearly on the 16 hour exposure referred to above. The long wave-length shift from λ4047 and the anti-Stokes lines from λ4078 and λ4358 appeared on plates exposed from 114 to 140 hours.

The existence of the 984 cm^{-1} vibration frequency is indicated by the appearance of Raman lines on the long wave-length side of λ4078 and λ4358 and by the appearance, on long exposures, of a line 989 cm^{-1} to the short wave-length side of λ4078. Although no clear indications of the 984 cm^{-1} scattering appeared on plates of less than 70 hours exposure the conclusion can not be drawn that this vibration frequency is more weakly scattered than the others. Observation of this scattering from the more favorable exciting lines, λ3650 and λ3655, is precluded by the low ultraviolet transmission of our prisms. Likewise, scattering from λ4047 falls, fortuitously, midway between the pair of 3654 cm^{-1} Raman lines excited by λ3650 and λ3655, and can not be separately resolved.

A more detailed account of our investigations will be published elsewhere (probably in the Journal of the American Chemical Society). We will also include application of this data to the computation of the high temperature heat capacity curve of water vapor.

We are indebted to the Department of Physics of this university for the use of the spectrograph and for other facilities which were generously placed at our disposal.

HERRICK L. JOHNSTON
MARGERY K. WALKER
Department of Chemistry,
The Ohio State University,
January 7, 1932.

[1] Rasetti, Nature **123,** 757 (1929).
[2] Hettner, Zeits. f. Physik **1,** 345 (1920).
[3] Dennison, Rev. Mod. Phys. **3,** 289 (1931).
[4] Mecke, Phys. Zeits. **30,** 907 (1929).
[5] Doure and Kastler, Comptes Rendus **192,** 1721 (1931).

Additional Evidence for an Isotope of Hydrogen of Mass 2

The discovery of an isotope of hydrogen of mass 2 by Urey, Brickwedde and Murphy[1] has been confirmed by a study of the isotopic molecular ion $(H^1H^2)^+$ of mass 3 with a mass spectrograph. At first sight it might seem hopeless to attack the problem from this angle because of the high probability for the formation of the triatomic ion $(H^1H^1H^1)^+$, also of mass 3, a process which is well known to occur in experiments of this kind. It is assumed that such an ion is a secondary product and hence proportional to the square of the pressure if the pressure is low. Such an assumption is in accord with all the experimental facts.[2] The isotopic molecular ion $(H^1H^2)^+$, however, should be formed directly from the normal (H^1H^2) molecule and should therefore vary in intensity as the first power of the pressure. Hence if the pressure is small enough the intensity of the $(H^1H^1H^1)^+$ ion relative to the $(H^1H^2)^+$ ion will be reduced to such an extent that the latter will become distinguishable with a sensitive apparatus.

A mass spectrograph was constructed, not primarily with the anticipation of working on this particular problem, but with the expectation of studying gaseous ions at very low pressures. The design is somewhat after the style of one previously built by the author.[3] In this case however a much larger solenoid was available making it possible to use the semi-circular type of analyzer. With this type of apparatus good intensity may be achieved at pressures ranging from 10^{-5} to 10^{-6} mm Hg.

Through the kindness of Professor Urey a sample of the residue of hydrogen which had been evaporated near the triple point by Dr. Brickwedde was placed at the disposal of the author. Two runs were made studying the intensity of the ions of mass 3 as a function of pressure, the first with ordinary hydrogen and the second with Brickwedde's concentrated sample. The hydrogen was allowed to leak through a fine capillary and flow continuously through the tube. The relative pressures were measured by using the tube as an ionization gauge.

The results of these two runs showed a marked increase in the number of ions of mass 3 in the concentrated sample as compared to the number in ordinary hydrogen, amounting, at some pressures, to as much as tenfold. The difference between the two curves was a linear function of the pressure and represents, it is believed, the increase in the relative numbers of (H^1H^2) due to the concentration process. If this is true then the measurements indicate a value for the abundance of (H^1H^2) as compared to (H^1H^1), as they existed in the concentrated sample under the conditions of the experiment, of 1/550 or an atomic ratio of 1/1100. The error in this value is probably not greater than 10 percent. In arriving at this figure it is assumed that the probabilities of ionization for the two diatomic molecules are the same.

The author is particularly grateful to Dr. Brickwedde of the Bureau of Standards for the preparation of the sample of hydrogen which made this investigation possible.

WALKER BLEAKNEY
(*National Research Fellow*)
Palmer Physical Laboratory,
Princeton, New Jersey,
January 9, 1932.

[1] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Bull. Amer. Phys. Soc. New Orleans Meeting, December 1931.

[2] H. D. Smyth, Revs. Mod. Phys. **3,** 357 (1931).

[3] W. Bleakney, Phys. Rev. **34,** 157 (1929); **35,** 139 (1930).

A New X-Ray Non-Diagram Line

Duane (Phys. Rev. **37,** 1017, 1931) mentions the existence of a very faint unidentified line between γ and β found in some of his long exposure photographs of the molybdenum K spectrum.

During a study of the δ and γ lines with a new type of double-crystal x-ray spectrometer a very faint line lying roughly midway between the γ and β_1 lines was found in the spectra of molybdenum, rhodium, palladium and silver. For convenience in this letter I shall call this line β_4. Its position checked, in molybdenum, with Duane's faint line as nearly as could be measured on a photograph which he had kindly sent me.

By interpolation, with I.C.T. values of $K\beta_1$ and $K\gamma$ the values of λ and ν for β_4 given in the tables below were obtained. It at once became evident that β_4 must originate in a transition from either M_{33} or M_{32} to K. No other upper level would even approximately satisfy the conditions.

	$\lambda\beta_4$(x.u.)	$\nu\beta_4$	$\nu K\alpha_1+\nu L\alpha_1$ $M_{33}-L_{22}-K$	$\nu K\alpha_2+\nu L\beta_1$ $M_{32}-L_{21}-K$	$\nu K\alpha_1+\nu L\alpha_1$ $M_{32}-L_{22}-K$
Mo	625.66	1457.1	1457.01	1456.79	1456.83
Rh	539.81	1688.9	1688.42	1688.02	1688.09
Pd	515.65	1768.0	1769.48	1769.26	1769.09
Ag	492.17	1852.4	1852.92	1852.49	1852.49

Whether the transition is to be regarded as a single drop $M_{33}-K$ (or $M_{32}-K$) or as a double electron drop in quick succession of the type ($L_{22}-K$, $M_{33}-L_{22}$) or ($L_{21}-K$, $M_{32}-L_{21}$) or ($L_{22}-K$, $M_{32}-L_{22}$) is at present a matter of personal preference. A single drop transfer of this general type is already known in the x-ray L region. The non-diagram line $L\beta_9$ (Siegbahn) is a transition $M_{33}-L_{11}$ and the line $L\beta_{10}$ is a transition $M_{32}-L_{11}$.

The intensity of $K\beta_4$ in molybdenum and rhodium is of the order of 1/1000 that of $K\alpha_1$. In palladium the intensity of β_4 has increased to 1/250 of α_1, and the line has become wider and distinctly unsymmetrical indicating a fainter component on the long wave-length side and about 0.15 x.u. distant.

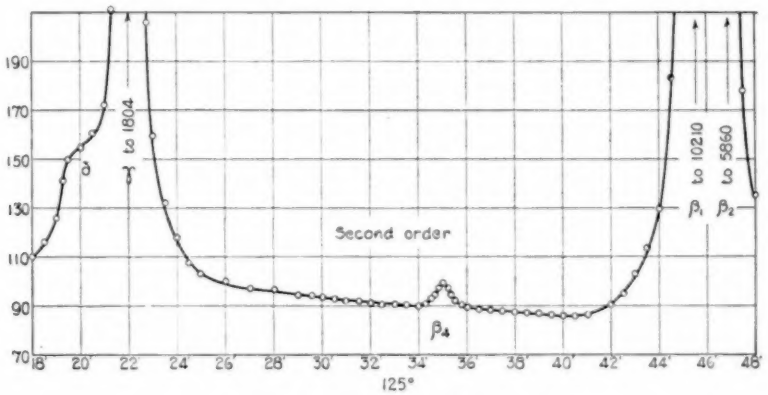


Fig. 1. Rhodium, 90 k.v., 27 m. a, 40 sec.

P. A. Ross

Department of Physics,
Stanford University,
January 12, 1932.

The Crystal Structure of Magnesium Platinocyanide Heptahydrate

The crystal structure of $MgPt(CN)_4\cdot 7H_2O$ has been examined by Bozorth and Haworth,[1] who concluded on the basis of their data, obtained from Laue and reflection photographs, that the Mg and Pt atoms were arranged in parallel rows so that the two kinds of atoms alternated with each other in the same row, the distance between their centers being 1.57A.

More recently one of us[2] has formulated the principles governing the structure of complex ionic crystals and of crystals containing electron-pair bonds. Application of these principles to $MgPt(CN)_4\cdot 7H_2O$ showed either that the principles must be modified or that the arrangement of Mg and Pt atoms in these crystals was not that supposed by Bozorth and Haworth. This led us to examine some of the more unsymmetrical Laue photographs in a search for spots which could not be accounted for by the structure assigned. These photographs were taken at the same time as the three used in the original structure-determination but were not analyzed at that time.

On one of the three additional photographs recently analyzed there is one diffraction spot inconsistent with the previously assigned body-centered unit of structure, and on another are eleven spots nine of which lie in the zone [100]. The planes responsible for

[1] Bozorth and Haworth, Phys. Rev. [2] **29,** 223 (1927).

[2] Linus Pauling, J. Am. Chem. Soc. **51,** 1010 (1929); **53,** 1367 (1931).

these eleven spots, and the wave-lengths of the x-rays (in A) calculated on the basis of the unit assigned by Bozorth and Haworth are: (03$\bar{1}$), 0.40; (041); 0.32; (04$\bar{1}$), 0.39; (061), 0.28; (0.6$\bar{1}$), 0.33; (081), 0.24; (08$\bar{1}$), 0.27; (0·12·1), 0.18; (0·12·$\bar{1}$), 0.19; (2$\bar{6}$3), 0.17: and (2$\bar{6}\bar{3}$), 0.22. Since the smallest wave-length consistent with the voltage on the x-ray tube is 0.21A, the above data show both that this unit must be doubled in the direction of the c-axis and that the lattice is not body centered. The correct unit has the dimensions 14.6 $\times$14.6$\times$6.26A^3 containing four molecules, and has a simple tetragonal lattice. The space-group cannot be determined because of the faintness of crucial reflections. On account of the relatively large reflecting power of the Pt atoms, the x-ray data indicate that these atoms are in the positions previously assigned; 0 0 0, $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{4}$, 0 0 $\frac{1}{2}$, $\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{4}$, referred to the new unit. Application of the principles mentioned above indicate that each Pt atom is surrounded by 4 CN groups at the corners of a square, a configuration similar to that of $PtCl_4$ in K_2PtCl_4,[3] and that the Mg atoms are not between the Pt atoms as previously supposed.

RICHARD M. BOZORTH

Bell Telephone Laboratories,
New York, N. Y.

LINUS PAULING

California Institute of Technology,
Pasadena, Calif.,
January 13, 1932.

[3] R. G. Dickinson, J. Am. Chem. Soc. **44,** 2409 (1922).

Note on the Spectrum of Sb II

An analysis of the first spark spectrum of antimony has been in progress for more than a year and it is hoped to make a full report on the work shortly when more accurate wave-length measurements now in progress have been completed.

This spectrum consists of a large number of lines extending throughout the entire range from the infrared to well below 1000A. The two active p electrons give a set of deepest terms, $^3P^1D^1S$, which have their strongest combinations throughout the Schumann region, some 25 of which have been located.

Since the second spark spectrum, which was reported on previously,[1] also has many of its strong lines in this region, I am re-examining this spectrum as well, not only to correct some known errors in the previous report, but also to extend it. To this end the entire Schumann region is being measured in the second or higher orders of the two-meter vacuum spectrograph against the standards of iron and neon. It is hoped in this way also to obtain some standard lines throughout this region which will be of greater accuracy than most of those in use at the present time

R. J. LANG

University of Alberta,
Edmonton, Canada,
January 14, 1932.

[1] Lang, Phy. Rev. **35,** 445–454 (1930).

Zeeman Effect of the Third Positive Carbon Bands

According to Asundi (Proc. Roy. Soc. **124,** 277, 1929) the third positive carbon bands, are ascribed to a $^5\Sigma\rightarrow{}^5\Pi$ transition. On the other hand, Birge, Mulliken and Weizel ("Bandenspektren" by Weizel p. 353 in 1st Supplement of the Wien-Harms "Handbuch der Experimentalphysik") postulate a $^3\Sigma\rightarrow{}^3\Pi$ transition.

It has been brought to the writer's attention (through the kindness of Professors Mulliken and Dieke) that a new rotational analysis of these bands will be published in the near future. Pending the assignment of rotational quantum numbers, the writer wishes to sketch qualitatively, the behaviour of the band-lines in a magnetic field.

The accompanying reproduction shows the bands near 2978A. The central part shows the Zeeman pattern, at 29,000 gauss, while the two outer portions are the no-field patterns (for purposes of comparison). The photograph (Fig. 1) was taken in the first order of a 21 foot grating.

All the band lines are strongly affected by the magnetic field, but the splittings or broadenings of lines are greater near the heads than at the higher rotational states. The second and third heads seem to be split into asymmetrical triplets with an over-all width of 5$\sim$6 cm^{-1}, while the over-all width of the

normal triplet at this field strength is equal to 2.7 cm^{-1}.

The assumption of a $^3\Sigma \rightarrow {}^3\Pi$ transition, with a $^3\Pi$ state intermediate between cases *a* and *b* should give for low rotational quantum numbers triplet groups of many lines each, with about double the normal Zeeman-triplet width, decreasing toward higher rotational quantum numbers, in agreement with the observations. A quantitative discussion of the patterns mentioned will be given when the above mentioned rotational analysis is published.

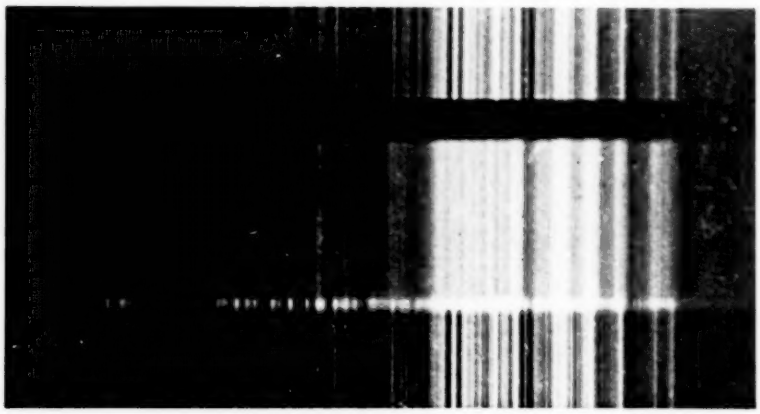


Fig. 1.

R. F. SCHMID
Rockefeller Foundation Fellow,
Ryerson Physical Laboratory,
University of Chicago,
January 15, 1932.

Excitation of the CO_2 Emission-Spectrum in a Back Box

Fox, Duffendack, and Barker (Proc. Nat. Acad. Amer. **13,** 302, 1927) reported on the excitation of CO_2 bands by electron-impact. Many band-heads were measured by them, and by Smyth (Phys. Rev. **38,** 2000, 1931). In the course of work on the Zeeman-effect of the third positive carbon group, it appeared that the entire CO_2 (or CO_2^+) band spectrum could be obtained in very considerable intensity from a Back box, with an arc current of about 0.5 ampere through streaming CO_2 gas. The bands were obtained in the first, second, and third orders of a 21 foot concave grating with less than 50 hours exposure, and the lines were sufficiently sharp to attempt a rotational analysis. Most of the band-groups, which are degraded toward the red, look like $^1\Sigma \rightarrow {}^1\Sigma$ of a diatomic molecule. This can be explained by assuming a linear model emitter.

However, the two bands at λλ2880A and 2895A show markedly different structure and behavior (see Duncan, Phys. Rev. **34,** 1148, 1929). These bands were also obtained with good intensity from the radiation of a graphite hollow-cathode (bore 4 mm in diameter, 30 mm long) although under these circumstances the red-degraded bands were considerably weaker. In comparing the pictures of the λ2880A bands taken from the Back box (at 29,000 gauss) and those from the graphite hollow-cathode, it appeared that the so-called *Q* branch (a sharp line in the middle of the bands) remained completely unaltered, while other parts of the band showed traces of magnetic effects. The writer is attempting a rotational analysis of the red-degraded simple system.

R. F. SCHMID
Rockefeller Foundation Fellow,
Ryerson Physical Laboratory,
University of Chicago,
January 15, 1932.

Specific Heat and Electronic Activation in Crystals

The magnetic[1] and optical[2] behavior of samarium ion (Sm^{+++}) in crystals shows clearly that Sm^{+++} possesses an electronic level little removed in energy from its basic level and that a considerable change in the relative populations of the two states is occurring near the temperature of liquid nitrogen. The determination of the specific heat of Sm^{+++} as a function of the temperature would then permit the study of an electronic transition in a crystal ascertaining the energy of activation, and the statistical weight of the excited electronic state, the basic state being regarded as known.

The method used in obtaining the electronic heat capacity of Sm^{+++} in $Sm_2(SO_4)_3 \cdot 8H_2O$ had some resemblance to that employed by Simon[3] and co-workers in separating the heat capacity due to excited states in solids from that expected from the heat capacity equations developed by Debye. The procedure followed in this research consisted however in making use of measurements made on a salt, $Gd_2(SO_4)_3 \cdot 8H_2O$, which should be expected to display very nearly the same specific heat as that of $Sm_2(SO_4)_3 \cdot 8H_2O$ in the absence of electronic excitation. The heat capacity measurements on $Sm_2(SO_4)_3 \cdot 8H_2O$ were made from 17°K to 125°K by employing the same method as described by Latimer and Ahlberg.[4] Data on the heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ over the same range of temperature were those of Giauque and Clark, as yet unpublished, and kindly furnished us by Professor Giauque. The two salts constitute neighboring members of a long series of isomorphous sulfates of the rare earth ions. These ions extend to both sides of Sm^{+++} and Gd^{+++} in the periodic table. It is well known that these ions differ very little in their strength of chemical binding, in volume, mass and other physical properties, except that the magnetic susceptibilities[5,6] and spectra[7] have established that practically all the ions of Gd^{+++} occupy the basic electronic state ($^8S_{7/2}$) from room temperature to that of liquid hydrogen. The difference in the specific heats would then give the net electronic specific heat of Sm^{+++} and consequently the energy required for the electronic transition (aside from a small correction arising from the lack of complete identity in the compressibilities, mass, etc., which we estimate to be negligible by means of the Madelung-Einstein-Grüneisen equation).

Preliminary measurements have shown conclusively that the difference in specific heats as a function of the temperature follows the Schottky[8] expression for transitions between quantum states

$$\Delta C_v = \frac{mR\left(\frac{h\nu}{KT}\right)^2 e^{h\nu/KT}}{(e^{h\nu/KT} + m)^2}$$

ΔC_v is the difference in specific heats at constant volume, m is the ratio of the statistical weights of the activated and the basic state, $h\nu$ is the energy of the transition, K is Boltzmann's constant, T is the absolute temperature, and R is the gas constant per mole. m was found to be 2 (i.e., 1.8 to 2.2) and ν was equal to about 160 cm^{-1}. There can be no question then concerning the reality of a large distribution between the two states at room temperature as the maximum number of ions participate in the transition at about 85°K.

This experimental work was performed almost two years ago at the University of California. Since then we have obtained much more accurate data, still uncalculated, which will be published in detail in the Journal of the American Chemical Society.

J. Elston Ahlberg
Simon Freed

Chemical Laboratory of the University of California,
George Herbert Jones Laboratory,
University of Chicago,
January 15, 1932.

[1] Freed, J. Am. Chem. Soc. **52,** 2702 (1930).
[2] Freed and Spedding, Nature **123,** 525 (1929).
[3] F. Simon, Ber. Berl. Akad. **33,** 477 (1926); F. Simon, Cl. v. Simson and M. Ruhemann, Zeits. f. physik Chem. **129,** 339 (1927).
[4] Latimer and Ahlberg, Zeits. f. physik. Chem. **148,** 464 (1930).
[5] Woltjer and Kammerling Onnes, Leiden Comm., 167C.
[6] Giauque, J. Am. Chem. Soc. **49,** 1870 (1927).
[7] Freed and Spedding, Phys. Rev. **34,** 945 (1929).
[8] Schottky, Phys. Zeits. **23,** 448 (1922).

BOOK REVIEWS

Der Smekal-Raman Effect. K. W. F. KOHLRAUSCH. Pp. viii+392; 85 figs. Verlag von Julius Springer, Berlin, 1931. Volume No. XII of the series "Struktur der Materie in Einzeldarstellungen", edited by M. BORN and J. FRANCK. Price, RM 33.80.

Physicists and physical chemists interested in the problems of the scattering of light by atoms and molecules and in the general problem of atomic and molecular structure will welcome this volume. It is a complete survey of the subject to date and investigators interested in this particular topic will find it very useful and satisfactory. The experimental side of this field of research in molecular structure is covered very satisfactorily and the theoretical aspects of the case are treated sufficiently so as to enable one to obtain a thorough knowledge of the Raman effect and to realize the great importance of this discovery by the Indian physicist. The book contains eight chapters and a table (51 pages) of Raman spectra discovered to date arranged in twenty-four groups which enable the investigator to find out about particular substances. A literature section contains 417 references and shows the large amount of work that has been done on the Raman effect since its discovery in 1928. The book can be highly recommended to all investigators and to anyone who wishes to obtain a more detailed knowledge of the Raman effect.

GEORGE GLOCKLER
University of Minnesota

Chemische Bindung als electrostatische Erscheinung. A. E. VAN ARKEL UND J. H. DE BOER. German Edition, authorized by the authors and translated by L. Klemm and W. KLEMM. Pp. ix+320; 71 figures. Verlag von S. Hirzel, Leipzig 1931. Price, RM 17.

This volume is an outstanding contribution to the literature of the subject "The Theory of Chemical Combination". No chemist should fail to study this book for it will give him an opportunity to bring his theoretical knowledge of "chemical combination" or "the chemical bond" up to date. Physicists will enjoy reading this treatise for they will find the treatment entirely to their liking. The whole subject is presented from the angle of physics, i.e., electrostatic theory. The following topics are treated in ten chapters: Ion-types; Molecules and crystals; Grating energies, electron affinity; Polarization; Molecular models; Deformation of ions; Volatility; Dipolemoment; Complex compounds; Hydration and solubility; Adsorption and crystal growth and many others. The book brings together all our knowledge of theoretical chemistry based on classical electrostatic theory. In other words it brings the subject to the era of "wave mechanics" (about 1926). Even these newer concepts are discussed in the last chapter, however very briefly, but properly so, for a complete treatment would most likely have doubled the volume. It is a great comfort to know that there is available now a book on the theoretical side of the subject of chemical combination that covers the period 1913 (Bohr) to 1926 (Schroedinger).

GEORGE GLOCKLER
University of Minnesota

Handbuch der Experimental physik. Hydre- und Aerodynamik, 1. Teil, Stromungslehre und allgemeine Versuchstechnik. Edited by L. SCHILLER. Pp. 730+xii, figs. 431. Akademische Verlagsgesellschaft, m.b. H., Leipzig, 1931. Price, RM 66.

This admirable compilation, edited by Ludwig Schiller, commences with an article by Ludwig Prandtl on fundamental ideas of the theory of the flow of fluids. Noteworthy features of the article are the remarks on the formation of vertices by the renewal of contact at the rear of an obstacle of two streams which were separated from one another at the front. There is also a good discussion of flow when the viscosity is very small, a subject in which the author was a pioneer. The nature of the flow round obstacles is beautifully illustrated by photographs obtained by illuminating particles suspended in water, the camera being in some cases stationary and in other cases in motion so that it follows the obstacle.

The article on classical hydrodynamics by H. Falkenhagen is particularly useful on ac-

count of the thorough presentation of hydrodynamical principles and equations, the discussion of the pulsating spheres of Bjerknes, the exposition of modern wing theory and the account of Oseen's improved derivation of the formula of Stokes for the viscous drag on a slowly moving sphere. The article also contains an excellent description by H. Schmiedel of different methods of making vortex motion visible. The pioneer work of Professor William B. Rogers is briefly mentioned and it may be interesting to recall Professor Trowbridge's remark that it is noteworthy that an account of the experiments of Rogers on the production of vortex rings in air and water was published in the very year that Helmholtz developed his celebrated theory. Rogers also studied the formations, analogous to mushrooms, which are produced by impulses too feeble to detach rings and observed a periodic distribution of analogous configurations at the boundary of the cylindrical jet produced by a continuous flow of fluid through the orifice at which the vortex rings are normally formed.

Schmiedel mentions some interesting experiments of Indra which indicate that elliptic vortex rings can be produced at an elliptic orifice by a strong impulse while a weak impulse produces two circular rings which move along diverging paths. The account of the behavior of pairs of vortex rings is pleasing and there is a particularly good account of the experimental work on vortex streets.

The important subjects of boundary layer theory and turbulent flow are ably treated by W. Tollmien who gives a clear and critical account of theoretical and experimental work, much of which has been done during the last few years. These articles will be of great value to men interested in aerodynamical and hydraulic research. One distinguishing feature is the attention given to mixing processes, particularly those at the boundary of a jet.

The article on the dynamics of gases by A. Busemann is extremely interesting from a mathematical standpoint. Interference pictures are used to show the nature of the flow in a jet when the velocity exceeds the velocity of sound in the gas. A clear exposition is also given of a graphical method of solving problems of flow of a compressible fluid at such high velocities. Ackeret's article on cavitation is welcome and timely. It commences with a theoretical study from physical and hydrodynamical standpoints of the conditions under which cavities form in a fluid. An account is then given of experimental methods for studying this phenomenon which has become one requiring speedy investigation on account of the erosion or corrosion of turbine and propeller blades. The article is well illustrated by means of diagrams and photographs showing the formation of cavities in the flow through nozzles and past wings. The article on the measurement of pressure by H. Peters deals with the Nipher collector, the Pitot and Venturi tubes and related instruments. The succeeding article by A. Betz describes the different types of micromanometers.

The subject of fluid meters is well treated by H. Mueller and H. Peters in an article which describes different types of measuring instruments, weirs, nozzles, plate orifices and so forth. The hot wire manometer, though mentioned in other articles, is treated in an exhaustive m nner in an article by J. M. Burgers. The book closes with a fine article by O. Tietjens on different methods of observing forms of flow. Particularly interesting methods are the method of striae and that depending on the use of oil drops having the same density as the liquid which is being studied. There are modern refinements, too, of the old methods of observing flow by means of particles suspended in the fluid. It is hard to say who first used these methods because they have been familiar ever since men observed rivers, clouds and smoke. An early use of them in the laboratory was made in 1843 by an American citizen Dyar when he studied solitary waves on the surface of water and showed by means of suspended dust particles that the motion is negligible at a depth below the surface equal to twice the height of the wave. Fumes of ammonium chloride were, on the other hand, used by Rogers in his early experiments on the production of vortex rings. In the more recent experimental investigations aluminum powder takes the place of suspended dust, the power being sometimes mixed with glycerine, and fumes of titanium tetrachloride take the place of fumes of ammonium chloride although in some cases they cannot be used with advantage on account of their corrosive action.

The writers of these articles seem to have studied conscientiously all the available literature and, considering the limitations of the average scientific library, have, on the whole, been very fair in ascribing credit to different authors. In few cases are laws or discoveries named after

particular scientists. This is, perhaps, wise, for, unless there is international agreement on such matters, some injustice may be done. A case in point is the familiar 'law of Poiseuille' which governs the slow flow of a fluid in a capillary tube. This is now called the Hagen-Poiseuille law on account of the experimental work of G. Hagen, which preceded that of Poiseuille as regards actual publication, but it may be argued that the law should really be called Navier's law because in 1822 Navier formulated the equations of motion of an incompressible viscous fluid and determined mathematically the rate of slow uniform motion of such a fluid in a fine tube on the assumption that the velocity was zero at boundary of the fluid, i.e. where the fluid meets an exceedingly thin adsorbed layer of fluid held stationary by the wall of the tube. Navier, moreover, compared his theoretical results with the experimental results of Girard which preceded those of Hagen and Poiseuille by nearly twenty five years. It is true that Navier worked out his theory for a tube of rectangular section and that the law of flow had been practically stated by Girard, though he did not really prove it, but the main point is that Navier correctly formulated a law of drag for capillary tubes involving the first power of the mean velocity and the coefficient μ in Newton's law of attrition which he generalised in such a way that μ could be determined in other ways and so provide numerical tests of the theory. The name of Poiseuille has been abbreviated for a unit of viscosity, that of Hagen might justly be used in connection with the dependence of viscosity on temperature but the law of flow in capillary tubes should be named for Navier unless it is named for Girard whose experiments produced results so interesting to physicians, chemists and mathematicians that they led Navier to make his immortal discovery of the equations of motion of a viscous fluid.

H. BATEMAN
California Institute of Technology

Physics of the Earth. IV. The Age of the Earth. Bulletin 80 of the National Research Council of the National Academy of Sciences, Washington, D. C. by ADOLPH KNOPF, E. W. BROWN, ARTHUR HOLMES, A. F. KOVARIK, A. C. LANE, and CHARLES SCHUCHERT. Pp. 485. Price $5.00.

The authors of this Bulletin constitute the subsidiary Committee on the "Age of the Earth" of the Division of Physical Sciences which has had the cooperation of the Division of Geology and of the American Geographical Union.

In a brief introduction, Knopf summarizes the principal results of the work of the subcommittee. In Part I, Schuchert presents the evidence for the age of the earth based on sediments and life. In Part II, Knopf discusses the age of the ocean in which he explains the apparently younger age as calculated from accumulation of salt in the ocean as due to loss of salt by adsorption and base exchange and to a present rate of salt supply much greater than the total average.

In Part III, Kovarik gives a very careful discussion of the methods of calculating the age of minerals from the data and principles of radioactivity. The lead accumulation method is the principal one. It is complicated by the fact that lead of different atomic weights is being accumulated from uranium, thorium, and actinium which is added to any original lead present or which may have been added later. All of these factors are dealt with in adequate detail.

Part IV which constitutes about half of the book is a splendid review by Arthur Holmes of the entire relationship between radioactivity and geological time. He considers the lead, helium and halo methods in all of their varied aspects and gives a remarkedly complete and able review of the entire field. In part V, E. W. Brown discusses briefly the indirect bearing of astronomical data on the earth's age.

On reading these very valuable contributions which approach a common focus from many widely varying angles, one cannot fail to be impressed by the rapidity with which modern science brings the newest discoveries to aid in solving its problems in quite different fields. The superior validity of the radioactive method of age determination seems to be firmly established and the object of comparison with the older methods is no longer to test the new method but to adjust the other time scales to accord with it by suitable explanation of the supposed discrepancies.

S. C. LIND
University of Minnesota

The Nature of a Gas. LEONARD B. LOEB. Pp. 134, figs. 11. John Wiley and Sons, 1931. Price, $2.50.

This monograph is the first of a series to be published by the National Research Council on Electrical Insulation. In the introduction Professor Loeb states that "in order, therefore, to understand the nature of a gas, so that we may study its electrical behavior, we must investigate first the nature of the atoms and molecules, as units, and then organize these structures, in their complex behavior, into a whole, comprising in its properties the condition of matter termed the gaseous state. In doing this it will be necessary for the sake of brevity to forego a historical or experimental analysis of the progress of the investigations during the last fifty years which led to our knowledge, and to state, in a clear and consistent form, merely the concepts and mechanisms to which we have been led by these discoveries." And it may be said that the author has done this very satisfactorily and concisely. The nature of the atom itself, the nucleus and extra-nuclear electronic distribution, is first described. The chemical behavior of the atom is presented as being "governed by the tendency of the outer electrons of atoms to reach dynamic stability by joining forces with electrons in similar or different atoms to achieve stable electronic configurations". The physical nature of a substance, as to whether it be in the solid, liquid or gaseous state, is very well discussed in terms of the fields of force existing between the atoms and molecules concerned. The kinetic picture of a gas is next considered, and the law of equipartition of energy is dwelled upon at considerable length. Finally, ionization phenomena in gases are considered. This includes a description of such processes as ionization by positive ions and by temperature, electron impact phenomena, photoelectric processes in gases, and inelastic impacts of the second kind.

The book is very well written. The material is clearly and simply presented; the author does not presuppose an extensive knowledge of the literature. There are a few misprints. In particular, it is strange that the numerical value ascribed to h is wrong in both the places that it is given! It is correctly recorded in the appendix, however. The appendix also includes a number of references.

R. RONALD PALMER
University of Minnesota

ERRATUM

Die elliptischen Funktionen von Jacobi. MILNE-THOMSON. Pp. 69, figs. 3. Julius Springer, Berlin 1931. Price RM 10.50. Reviewed by W. E. Milne, Phys. Rev. **38,** 1913 (1931).

In the next to last paragraph read "Weierstrass p-function" for "Weierstrass θ-function."

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

MINUTES OF THE BERKELEY MEETING, DECEMBER 18–19, 1931

The 174th regular meeting of the American Physical Society was held in Room 212 LeConte Hall, University of California, on Friday December 18, 10:00 to 12:30 and 2:00 to 4:30, and on Saturday December 19 from 10:00 until 11:30. There were some 50 members of the Physical Society in attendance with a program of 28 papers presented, of which numbers 21 to 28 inclusive, were on the supplementary program.

The meeting was called to order by Local Secretary for the Pacific Coast. Professor E. E. Hall, Chairman of the Department of Physics, University of California, was duly elected Chairman for the session and presided. There was no business of importance to present to the Society and no business was transacted.

The members of the Physical Society assembled at luncheon at the Faculty Club of the University of California at noon on Friday and Saturday. On Friday evening there was an informal dinner for visiting members of the Physical Society at the Faculty Club. There were tours of inspection of the researches in progress on Friday afternoon and Saturday morning and afternoon following the close of the session.

The program of presented papers is given in the following abstracts of which papers numbered 15, 19 and 20 were read by title. By vote of the Society papers 8 and 10 were given consecutively and papers 23 and 24 on the supplementary program followed paper 7 in the session of Friday morning. Supplementary papers 25 and 26 followed paper 14 at the end of the session of Friday afternoon. Paper 27 on the supplementary program was presented at the beginning of the Saturday morning session following paper 15, which was read by title. Paper 27 was accompanied by an actual demonstration of the high speed diffusion pump. Paper 16 and paper 21 of the supplementary program were combined and presented subsequent to paper 20 on the Saturday morning program by a vote of the Society, followed by paper 28.

LEONARD B. LOEB

Local Secretary for the Pacific Coast

1. The silvering of Fabry-Perot etalons by evaporation. H. E. WHITE AND S. S. BALLARD, *University of California.*—The method used is essentially that developed by R. Ritschl at the Physikalisch-Technische Reichsanstalt. The chief alteration from Ritschel's method is in the manner of vaporizing the silver. Here a method developed by Cartwright and Strong is em-

ployed. Instead of using a single filament of silver wire, a conical shaped molybdenum filament is used. Silver in the form of a small bead is placed inside the filament in contact with the molybdenum. Upon passing a sufficiently high current through the filament the silver is melted and brought almost to the boiling point where it vaporizes rapidly. With the etalon plates 15 cm from the filament two uniform films of the required thickness are obtained simultaneously in from one to five minutes. The pressure in the chamber is such that the mean free path is greater than the plate-filament distance. An optical pyrometer is used to determine the thickness of the silver film as it deposits, and the process is stopped when films of the desired transmission are obtained. This and the uniformity of the films obtained are the chief advantages over sputtering methods. In favorable cases etalons have been obtained where, with the filament of a 100 watt lamp as an object, 50 images at 6000A are seen with the eye. These etalons are being used in photographing hyperfine structure. In order to obtain resolving power in the ultraviolet, attempts will be made to adapt this method to the evaporation of platinum.

2. Photoelectric properties of thin films of rubidium and caesium on silver. JAMES J. BRADY, *University of California.*—By the use of a molecular beam a computed number of alkali metal atoms were deposited on a silver surface cooled with liquid air. The method was described by the author in a report (Phys. Rev. **37,** 230 (1931)) on the study of potassium films. The vapor pressures of rubidium and caesium for various temperatures were determined from data given in the International Critical Tables (Vol. 3, page 205). Spectral response curves were taken for various film thicknesses. The maximum threshold (approximately 6200A) in the case of rubidium was found to exist at a film thickness of 1.5 molecular layers (7.3×10^{14} atoms per cm^2). The maximum photoelectric emission occurred at a film thickness of 5.0 molecular layers and the photoelectric properties did not change when the film thickness was increased beyond 12 molecular layers. The threshold for the thick film was approximately 5900A. For caesium the maximum threshold, approximately 6600A, was found at a film thickness of 1.5 molecular layers (6.3×10^{14} atoms per cm^2). The maximum emission occurred at 5.4 molecular layers and the photoelectric properties remained constant for film thicknesses greater than 10 molecular layers. The threshold for the thick film was approximately 6300A. A theory is proposed which accounts for the existence of a maximum in the excursion of the long wave-length limit.

3. Monochromatic de Broglie waves of molecular beams. I. ESTERMANN, R. FRISCH AND O. STERN (Introduced by L. B. LOEB.), *University of Hamburg.*—An ordinary molecular beam of He which contains molecules of all velocities according to the Maxwell distribution law and consequently a continuous spectrum of de Broglie waves, passed through a system of rotating toothed wheels. By this means monochromatic molecular beams containing only molecules of distinct ranges of velocities were produced. These beams were diffracted by the crossed-grating of the surface of a LiF crystal. The de Broglie wave-lengths of these beams calculated from the grating constant of the LiF crystal and the diffraction angles were in complete agreement (within a limit of 1 percent) with the wave-lengths calculated with de Broglie's equation $\lambda=h/mv$, v being determined from the dimensions and number of revolutions of the toothed wheels. The relative intensities of monochromatic beams of different wave-lengths were found to correspond to Maxwell's distribution law of velocities.

4. Absolute values for the mobilities of gaseous ions in pure gases. N. E. BRADBURY (Introduced by L. B. LOEB.), *University of California.*—With the method of Tyndall and Grindley adapted to a baked-out glass ionization chamber with an external source of intense x-ray ionization, the absolute values of the ionic mobility have been determined for several gases under conditions of high purity. Air was passed through a carefully constructed purifying train and liquid air traps. The absolute values of the mobilities found in this case were 1.60 and 2.21 for the positive and negative ion. Oxygen was prepared by fractionation of tank oxygen, by heating potassium permanganate, and by heating potassium chlorate. The first two of these methods gave 1.58 for the positive ion and 2.18 for the negative. The oxygen from potassium chlorate, however, showed an anomalous high mobility for the negative ion, values as high as 2.65 being obtained. The presence of chlorine oxides from the decomposing chlorate may be responsible for this. Nitrogen was obtained from a commercial tank and by heating sodium azide. The former method, even after passing the gas through the purifying train gave only 30 percent

free electrons, a negative ion of mobility 2.21, and an abnormally high positive value of 1.82. Nitrogen from sodium azide gave no negative ions and 1.62 for the positive ion. Hydrogen was obtained from a commercial tank source, gave no negative ions, and showed a positive mobility of 8.25 with indications of the higher mobility ion observed by Loeb (Phys. Rev. **38**, 549 (1931)) with a mobility of 13.1. Helium, purified by passing through charcoal traps in liquid air gave on preliminary measurements a main mobility of 7.1 and an ion of high mobility 17.3 in agreement with values observed by Tyndall and Powell (Proc. Roy. Soc., **129**, 162 (1930)). No negative ions could be detected in the gas. Especially purified helium sparked over magnesium gave only the positive ion of mobility 17.

5. The collision cross-section of argon atoms for 300 to 2500 volt electrons. ROBERT B. BRODE, *University of California.*—A beam of electrons was defined by three slits set 90° apart on a circle 3 cm in radius. The first slit was 0.1 mm wide and the other two were 0.4 mm wide. The magnetic field of a large solenoid bent the electrons into this path and at the same time determined their velocity. The total cross-section of argon atoms that was effective in removing electrons from this beam was found by observing the decrease in current at the end of the path as a function of the gas pressure. When the current in the beam was over 10^{-7} amperes the current at the end of the path was not proportional to the current which started in the path. This variation was due to ionization along the beam and its effect was eliminated by using currents of 5×10^{-9} amperes. The curve of the cross-section plotted as a function of the velocity of the electrons decreases a little more rapidly than inversely proportional to the velocity. Small changes in slope appear at 24, 35, and 45 (volts)$^{1/2}$. The following table gives the values of q, the total collision cross-section in cm^2, and α, the absorption coefficient, which is the number of collisions per cm path at 1 mm pressure experienced by each electron.

(volts)$^{1/2}$	20	25	30	35	40	45	50
$10^{16}\times q$	2.98	2.17	1.69	1.24	1.01	.78	.65
α	10.7	7.80	6.08	4.45	3.62	2.84	2.35

6. Probable values of e, h, e/m and α. RAYMOND T. BIRGE, *University of California.*—The possibility of the simultaneous evaluation of e and h, from the totality of experiments designed to measure h, as discussed by Bond (Phil. Mag. **10**, 994, 1930 and **12**, 632, 1931) is of the utmost importance. This is potentially a far more reliable method for the evaluation of e than any direct determination. The writer, however, disagrees with Bond's selection of data, with some of his calculations and with all of his final results. In particular, Bond's calculated errors are incorrect, due apparently to the use of least squares' formulas not applicable to the situation. The writer now presents a critical re-examination of available data, together with a discussion of the various least squares' formulas required in this rather unusual type of calculation. The resulting values of e and h are found to depend chiefly upon the value adopted for e/m. With $e/m=1.761\times10^7$, which now seems well established, I obtain $e=(4.7721\pm0.0036)\times10^{-10}$, $h=(6.552\pm0.007)\times10^{-27}$, $1/\alpha=137.28\pm0.07$. This value of e is considered more reliable than any previous direct determination. If $1/\alpha$ equals 137 exactly (Eddington's theory), then e/m must equal 1.768×10^7 approximately, and this value now seems quite improbable.

7. On the dependence of the length of the ultra-short electromagnetic waves upon the heating current of the tube and upon the amplitude of the oscillations. G. POTAPENKO, *California Institute of Technology.*—Previous work of the author has shown (Phys. Rev. **38**, 584, 1931), that a vacuum tube may generate oscillations, the frequency of which exceeds many times the frequency of electronic oscillations around the grid. Ultra-short "dwarf" waves of a few centimeters wave-length were obtained by means of this method. Experiments have shown that the frequency of "dwarf" waves are not exact multiples of the frequency of the electronic oscillations as might be expected. The theory proposed by P. S. Epstein shows that this discrepancy may be explained by the influence of the amplitude of the generated oscillations upon the movement of the electrons around the grid. Investigations of the dependence of the lengths of the generated waves upon the heating current of the tube and upon the amplitude of oscillations completely confirmed the prediction of this theory.

8. The x-ray determination of the thermal expansion of Bi single crystals. A. GOETZ AND R. C. HERGENROTHER, *California Institute of Technology.*—The value of the thermal expansion coefficient parallel to the principal axis of Bi-crystals ($1/l_{\parallel} \cdot dl/dT = \alpha_{\parallel}$) has been determined by the measurement of the angles of Bragg reflections of the higher orders of Mo-Kα-radiation from the (111) plane, between room temperature and the melting point (272°C). The accuracy of this determination is of the same order as macroscopic measurements of expansion. The observations were made in order to compare the results with the macroscopic measurements of $\alpha_{\parallel}$ and $\alpha_{\perp}$ by Bridgman and Roberts. The decline of the macroscopic expansion 30°−40° before the melting point could *not* be found by x-rays proving that the crystal elements do not disintegrate before the point of fusion occurs. The values of $\alpha_{\parallel}/c_p$ (c_p=true specific heat) show furthermore a striking constancy over the range of temperature measured, whereas this ratio shows variations with temperature up to 100 percent for the macroscopic expansion. The difference between macroscopic and x-ray observations seem to indicate the existence of a secondary structure which begins to yield gradually before the melting point of the crystal element. Certain irregularities of the temperature dependence of the reflected intensities seem to strengthen this explanation. The mean value for $a_{\parallel}$ between 20° and 272° as obtained by x-rays is 16.1 $\times 10^{-6}$ cm deg^{-1} which agrees with the macroscopic observation of Roberts (16.2×10^{-6}).

9. The momentum of a moving body in special relativity. W. V. HOUSTON, *California Institute of Technology.*—It is often difficult to visualize the nature of the added momentum given to a moving body by a uniform pressure acting on it. A simple picture of this effect may be constructed in the case of a perfect gas enclosed in a moving container. When viewed by an observer who is at rest with respect to the box, the molecules appear to be uniformly distributed among the different possible directions of motion. However, to an observer past whom the container is moving, more molecules are moving with the box than against it. This does not affect the total energy which is simply the scalar sum of the individual energies. It does, however, affect the momentum which is the vector sum of the individual momenta, and produces the extra term which involves the momenta.

10. Metamagnetism in Bi single crystals. A. B. FOCKE AND A. GOETZ, *California Institute of Technology.*—The influence of the presence of foreign atoms within the lattice of Bi crystals upon the magnetic susceptibility ($\chi_{\perp}$ and $\chi_{\parallel}$) is studied for the cases of Bi-Pb, Bi-Sn and Bi-Ge. In all cases the foreign atom is enantiomorphic and thus cannot replace a Bi atom. As long as the concentration is below the solubility limit (0.5 to 5 percent) foreign atoms always cause an increase of the magnetic anisotropy as well as an increase of its temperature coefficient. Thus the normal anisotropy of pure Bi crystals ($\chi_{\perp}/\chi_{\parallel}=1.425$) (A. B. Focke, Phys. Rev. **36,** 319, 1930) can increase in case of a tin concentration at the solubility limit (*ca.* 3 percent) to values of 10^4. (A. Goetz and A. B. Focke, Phys. Rev. **38,** 1569, 1931.) At lower temperatures $\chi_{\parallel}$ decreases to zero and below −3°C the crystal is paramagnetic parallel to the axis and stays diamagnetic normal to it. Measurements of the quantitative effect of concentrations of foreign atoms (beginning at 0.005 percent Pb) yielded the following empirical formula for the inverse magnetic anisotropy of Bi:

$$\chi_{\parallel}/\chi_{\perp} = R = R_0 - (\beta_0 + \alpha_0 \cdot N^{\phi}) \cdot (T_0 - T) \cdots$$

where T=abs. temperature; T_0=temperature at which the influence of foreign atoms upon the anisotropy disappears; $R_0=R$ for $T=T_0$; β_0=temperature coefficient of R for purest Bi; N=concentration of foreign atoms; α_0=effect of one foreign atom upon R; $\phi=(N/\alpha)\cdot(d\alpha/dN)$. The values obtained for Bi are $T_0=813° \pm 5°$ abs.; $R_0=0.95$; $\phi=0.5 \pm 0.005$. Hence α is the only constant which depends on the type of impurity. Pb and Sn follow the relation over the whole range of temperature, whereas Ge shows at high temperatures deviations which seem to indicate the formation of an intermetallic compound.

The influence of dissolved foreign atoms is too large to be accounted for in terms of a statistical volume distribution. It seems necessary to assume an adsorption in the internal surface of the crystal due to the boundaries of its secondary structure. Approximate calculations give the same value for the parameter of this structure (*ca.* 10^{-4} cm) as was previously observed. (Goetz, Proc. Nat. Acad. **16,** 99, 1930.)

11. Soft x-ray critical potentials of beryllium. R. J. CHRISTENSEN (Introduced by R. B. BRODE.), *University of California.*—Soft x-ray critical potentials up to 250 volts have been observed for freshly distilled Beryllium surfaces, observations being taken with the general type of tube employed by Richardson and his collaborators. When the photo current per unit bombarding current is plotted directly against the accelerating potential a number of points are discernable at which the slope of the curve abruptly changes. The considerably strongest break, occurring at 112.8 volts, is attributed to K radiation. In comparison the spectroscopic data of Söderman (Zeits. f. Physik **65**, 656) show for the K radiation a width of 12 volts, the short wave-length limit corresponding to 112 volts. The width is explainable by the broadening of the energy states for the atom within the metal. The value obtained by the critical potential method must correspond to an energy somewhat higher than the spectroscopic value, the reason being that the bombarding electron must possess sufficient energy to remove the K electron up to at least the lowest allowed energy state in the metal, which is probably among the upper Fermi states, and in addition retain sufficient energy to be in another, likewise allowed state; while the radiation emitted is for the most part due to transition into the K states from states of less energy than the higher Fermi states. Two other rather strong breaks occur at 9.3 and 11.7 volts. These may be ascribed to transitions from the Fermi group to possible discrete L levels. Other weaker break points are found at 18.7, 25.7, 33.7, 45.5 and 123.9 volts. A large number of very weak breaks of a rather unrepeatable nature are also observed.

12. Predissociation in the sulfur monoxide molecule. E. V. MARTIN AND F. A. JENKINS, *University of California.*—The ultraviolet SO bands, first described by Miss Lowater in 1906, and later studied by Johnson and Cameron and by Henri, have now been photographed in the second order of the 21-foot grating. Measurement and analysis of the rotational structure of five bands completely confirms their $^3\Sigma \rightarrow {}^3\Sigma$ character, and yields the following preliminary molecular constants: $\nu_e = 39{,}362.6$, $\Delta G_v' = 628.7 - 11.3(v' + \frac{1}{2})$, $\Delta G_v'' = 1124.97 - 12.287(v'' + \frac{1}{2})$, $B_v' = 0.501 - 0.006(v' + \frac{1}{2})$, $B_v'' = 0.7055 - 0.00505\ (v'' + \frac{1}{2})$, $I_e' = 55.21 \times 10^{-40}$ g·cm², $I_e'' = 39.21 \times 10^{-40}$, $r_e' = 1.771 \times 10^{-8}$ cm, $r_e'' = 1.493 \times 10^{-8}$, $\gamma'' \backsim 0$, $\gamma' = \pm 0.019$, $\epsilon' - \epsilon'' = -0.686$. The spin tripling is completely resolved above $K' = 30$, and can be studied to $K' = 66$. Perturbations occur in the upper states, and are particularly strong for $v' = 1$ and 2. A sudden breaking off of the rotational lines occurs for bands with $v' = 0$ at $K' = 66$, for $v' = 1$ at $K' = 52$, and for $v' = 2$ at still lower K'. The $v' = 3$ bands are very short, and no bands with higher v' are observed. This is readily explained as due to predissociation and leads to 5.10 ± 0.02 volts as the heat of dissociation of normal SO, in contrast to the value 6.41 obtained by Henri by linear extrapolation of the lower levels.

13. Mass ratio of the boron isotopes from the spectrum of BO. F. A. JENKINS AND ANDREW MCKELLAR, *University of California.*—Extensive measurements have been made of the α bands of BO as excited by active nitrogen. With the dispersion of the second order of a 21-foot grating, the data on the vibrational isotope effect permit a precise evaluation of the ratio of the reduced masses of $B^{11}O$ and $B^{10}O$, $\rho^2 = \mu/\mu^i$. The vibrational term-differences were found by applying the accurate methods developed by Birge in his work on the masses of the oxygen isotopes. Using the (0,0), (0,1) and (0,2) bands, we obtain by least squares $\rho = \omega_e^i/\omega_e = 1.029071 \pm 0.000046$. Entirely independent data from the (1,0), (1,1) and (1,2) bands give $\rho = 1.029087 \pm 0.000052$. The value of ρ corresponding to integral masses 11 and 10 is 1.029203. It is also found that the ratio of the band constants χ_e^i/χ_e equals ρ within the probable error, and that the requirement $\alpha^i/\alpha = \rho^3$ is satisfactorily fulfilled. Aston found the masses 11.0110 ± 0.0016 and 10.0135 ± 0.0015 with the new mass-spectrograph, which gives the ratio $B^{11}/B^{10} = 1.09962$, with a *limit* of error of ± 0.00032. Our mean ρ corresponds to 1.09961, with a *probable* error of ± 0.00006, for this ratio, assuming Aston's absolute value for B^{10}. This constitutes the first independent check on Aston's relative masses and shows them to be more accurate in this case than indicated by his limits of error.

14. Width of the D lines in sodium vapor. S. A. KORFF, National Research Fellow, *Mt. Wilson Observatory.*—Microphotometer contours of the D absorption lines of sodium vapor obtained with the 30-foot spectrograph at Mount Wilson show improved agreement with theory

over values previously obtained. The lines are somewhat too wide, to have been produced by classical radiation damping. It is difficult to see, under the experimental conditions employed what other processes might be involved. The temperature range studied was from 180° to 300°C, representing vapor densities of approximately 10^{12} to 10^{14} atoms per cc. Above the latter temperature, pressure broadening sets in. The 2:1 ratio between the D lines is obtained, as is the theoretical variation of width with the square root of the number of atoms in the absorbing column.

15. New measurements of the 1, 1 band of atmospheric oxygen. HAROLD D. BABCOCK AND WENDELL P. HOGE, *Mount Wilson Observatory.*—Previous measurements resulting in the discovery of the 1,1 band (Phys. Rev. **35**, 125, 1930) were made on a single plate. Eight new spectrograms, four from each of two excellent gratings, with solar zenith distances from 84° to 91° have now been measured. The increased air-path and improved photographic contrast permit measurement of 49 lines. These give within small errors of observation the same spacing of rotational levels of excited oxygen as we find from the B band, confirming Mulliken's interpretation of the atmospheric bands. The spacing of rotational levels of normal oxygen is systematically less for 1,1 than for A, B, and α bands, as would be expected. Taking separations of lines in P_1 and R_1 branches of 1,1 from homologous lines in the B band we find, after eliminating the rotational effect, that the first vibrational level of normal oxygen is 1556.393 ± 0.006 cm $^{-1}$ above the ground state. A small error is found in the earlier determination of this interval and allowance for this makes that value consistent with the new, more reliable result. The second doublet in the tail of 1,1 is closely matched in intensity by the eighteenth in the tail of 0,0.

16. Variation with temperature of the continuous absorption of light by diatomic gases. G. E. GIBSON, *University of California.*—Condon has shown that the continuous absorption arising from molecules in the lowest vibrational state ($v''=0$) should vary with frequency in the manner actually observed; the maximum in the vibrational wave function, giving rise to a maximum in the absorption coefficient. Extending his reasoning we should expect the absorption arising from molecules in the first vibrational state ($v'=1$) to give two maxima corresponding to the maximum and the minimum of the wave function. Corresponding to the single node of the wave function ($v'=1$) we should have zero absorption near the frequency for which the absorption from $v''=0$ is a maximum. This is qualitatively in accord with measurements by Bayliss on chlorine (not yet published). Near the maximum the absorption diminishes with temperature, owing to the decreasing number of molecules in the lowest vibrational state, while at frequencies farther from the maximum the increasing number of molecules in the first vibrational state causes the absorption to rise with temperature.

17. A double crystal x-ray spectrometer and spectrograph. P. A. ROSS, *Stanford University.*—A double crystal spectrometer has been built which seems to possess certain advantages in convenience of operation. The first crystal does not rotate but is moved along milled ways perpendicular to the midpoint of the line joining the focal spot to the axis of rotation of the second crystal. The beam reflected by the first crystal always passes over the axis of rotation of the second crystal which is mounted on the table of a large Bragg spectrometer equipped with a fine slow motion reading in seconds of arc. Both crystals and their fine adjustment controls are mounted on easily removable plates. Two taper pins in each plate provide for the accurate replacement of either crystal in its original position or turned through exactly 180°. The constants of the apparatus having been determined, the crystals may be removed and replaced, used in parallel or anti-parallel position, or as a single crystal spectrometer with no loss of time hunting for lines. By means of an electric rocking device, the apparatus has been used as a double crystal spectrograph showing the β doublet resolved and the γ and δ lines in molybdenum.

18. The effect of transverse magnetic fields on the thermal conductivity of bismuth at low temperatures. E. J. KNAPP, *University of Wisconsin.*—A vacuum conductivity method was employed to observe the thermal conductivity of polycrystalline bismuth in transverse magnetic fields ranging from zero to 11,000 gausses. Two series of observations were made. In the first series the average temperature of the specimen was −160°C; in the second series it was

−119°C. The variation of the relative decrease in thermal conductivity with magnetic field strength was found to fit the equation, $\Delta\kappa/\kappa = BH^2/(1+CH^2)$. The maximum decrease was 28.9 percent in the first series of observations and 24.0 percent in the second series. In the first series the point of inflection of the curve, $\Delta\kappa/\kappa$ against H, appeared at about one-ninth of the maximum field strength; in the second series it appeared at about one-fifth of the maximum field strength. This work is being extended to single crystals at the University of Wisconsin.

19. The spectra of two-and-three-valence-electron atoms. Si_{II}, P_{III}, S_{IV}, Si_{III}, P_{IV} and S_V. I. S. BOWEN, *California Institute of Technology.*—New measurements of the vacuum spark spectra of silicon, phosphorus and sulphur have been made with a vacuum spectrograph. With the aid of these data it has been possible to analyse a large number of hitherto unclassified lines as follows; in Si_{II}, P_{III} and S_{IV} many of the important quartet lines have been located. In Si_{III} and P_{IV} the stronger singlet lines have been classified, while in these ions and in S_V a large number of lines involving terms in which both electrons are excited have been identified.

20. Thermal expansion of copper alloys. PETER HIDNERT, *Bureau of Standards.*—The linear thermal expansion of two cast copper alloys was investigated. One alloy (sample 1444A) made by the Bunting Brass and Bronze Company contained copper 84.84, tin 14.95 and lead 0.21 percent and the other alloy (sample 1445) prepared at the Bureau of Standards contained copper 85.0, tin 5.0, zinc 5.1 and lead 4.9 percent. C. E. Eggenschwiler and H. B. Gardner determined the chemical composition of the first and second alloy, respectively. The following coefficients of expansion were obtained from the observations on heating.

Temperature range	Average coefficients of expansion per degree centigrade	
	Sample 1444A	Sample 1445
20 to 100°C	18.0×10^{-6}	17.8×10^{-6}
20 to 200	18.2	18.1
20 to 300	18.6	18.5
20 to 400	18.8	18.9
20 to 500	19.3	19.3
20 to 600	19.8	20.0
20 to 700	—	20.6

The results indicate that the substitution of about 5 percent zinc and 5 percent lead for 10 percent tin in the first alloy, caused slight if any changes in the coefficients of expansion.

21. Theory of the continuous absorption of light by diatomic molecules. G. E. GIBSON AND O. K. RICE, *University of California and Harvard University.*—The theory of the effect described in Abstract 16 has been developed on the basis of quantum mechanics, and is found to be in quantitative agreement with the observed absorption curves and temperature coefficients.

22. On the measurement of the energy of ultra-short electromagnetic waves. G. POTAPENKO, *California Institute of Technology.*—Because of the lack of methods for direct absolute measurement of the energy of ultra-short electromagnetic waves, the author proposes an approximate method of measuring the energy. This method is based on the determination of the amplitude of oscillations and of the current which appears in the plate circuit of the tube generating ultra-short waves. In this way the energy of "dwarf" waves (see previous abstract) has been measured and a method of increasing their energy by means of negative plate potential has been studied. The power of ultra-short waves generated with *one* amplifier tube can in this manner be brought up to 0.08 watts for wave-lengths of about 10 cm and up to 0.2 watts for wave-lengths of about 60 cm.

23. The calculation of errors by the method of least squares. RAYMOND T. BIRGE, *University of California.*—The assumptions underlying the various least squares' formulas for the calculation of errors are stated, and the true meaning and applicability of the formulas are critically discussed. New experimental data are presented which indicate the essential correct-

ness of the Gaussian error curve, in the region of large residuals as well as small. Scarborough's deduction (Proc. Nat. Acad. Sci. **15**, 665, 1929) that the calculation of errors from *internal* consistency is correct, but the calculation from *external* consistency is invalid, is shown to be entirely unjustified. Either method may be used, if only accidental errors are involved, and any serious disagreement of the two methods is a sure indication of the presence of constant or systematic errors. In this latter situation the error calculated from internal consistency is obviously untrustworthy, yet the literature abounds in examples of the use of such false errors,—notably in F. W. Clarke's extensive calculations of atomic weights. In this situation the only feasible procedure is to assign weights arbitrarily and calculate the error of the resulting weighted average by means of *external* consistency. The above conclusions are illustrated in detail, using actual observational data.

24. Nuclear spin of phosphorous from the band spectrum. F. A. JENKINS AND MURIEL ASHLEY, *University of California.*—The resonance band system of the P_2 molecule, first measured by Geuter, and recently studied by Herzberg and by Jakolewa (Zeits. f. Physik **69**, 548, 1931) has been photographed in emission with high dispersion. The rotational structure is well resolved in the region 2300–3300A, but overlapping is serious except for a few bands between 2700–3000. These show only P and R branches consisting of single lines, the structure characteristic of a $^1\Sigma \rightarrow {}^1\Sigma$ transition. Alternating intensities occur in each branch, and are particularly well marked in the band at λ2953.9, for which the P and R branches are approximately superimposed. This is the 6,22 band, according to Jakolewa's assignment of vibrational quantum numbers. A number of the neighboring bands have the two branches separated, and the alternation of intensities in each is definite. The alternation ratio observed visually appears to be 3:1, giving for the nuclear spin $I = \frac{1}{2}$. Until quantitative measurements are made, the ratio 2:1 cannot be definitely ruled out, although not expected theoretically for atoms containing an odd number of nuclear protons. A detailed analysis of the rotational structure of this band system is being undertaken.

25. The photoionization of atomic potassium. MELBA PHILLIPS, *University of California.*—The photoelectric yield in potassium vapor is found observationally to pass first through a minimum and then through a pronounced maximum (at 2480A) as the wave-length is decreased beyond the series limit. We have tried to see whether such behavior of the potassium atom could be understood. We have taken for the atomic field Hartree's self-consistent field, corrected for the polarization of the core to give correctly the term value of the normal state. The photoelectric intensity diminishes with decreasing frequency, as in the case of other atoms; the decrease is a good deal faster than that given by a λ^3 law; and no anomalous maxima appear. There seems to be no reasonable change in the atomic field which could give the observed curve. The absolute value of the absorption coefficient is smaller than that estimated experimentally by Ditchburn, and more than ten times smaller than the value for sodium. An appreciable part of the photoionization could thus be due to molecules, although under the conditions of the experiment relatively few such molecules have been supposed to be present. This possibility is being investigated.

26. The continuous radiation of slow electrons. LEO NELEDSKY, *University of California.*—The radiation of electrons in a Coulomb field has been computed by the correspondence principle and on the quantum mechanics; for fast electrons and high frequencies this model gives a satisfactory account of the production of continuous x-rays by electrons impinging on matter. For slow electrons and relatively soft x-rays the model fails, giving in all cases too much radiation. We have therefore refined the model, taking roughly into account the screening of the atomic electrons, by surrounding the nuclear point charge by a shell of negative electricity. As was to be expected, both for low velocities (under thirty volts), and for small velocity changes, this model gives much less radiation than that of the unscreened charge. A comparison of the theoretical isochromats with experimental ones recently obtained by Mohler and Boeckner shows agreement in the shape of the curves, and a very reasonable agreement in their absolute magnitude, whereas a correct application of the earlier calculations would fail to give these. For light atoms the curve of intensity of radiation plotted against the product of radius and mean charge shows striking maxima and minima.

27. Design of a high-vacuum, high-speed diffusion pump. HAROLD T. BYCK AND I. ESTERMAN, *University of California.*—By a combination of metal nozzle and glass body, a one-stage diffusion pump with a pumping speed equal to that of well-known three-stage metal pumps has been built. While the design involves no new principles, the combination of glass and metal is one which can be made easily and cheaply in any laboratory. The final design is the result of a series of measurements of pumping speed with variation of diffusion area, and the dimensions given yielded the maximum pumping speed which is of the order of 14 liters of air per second at 10^{-3} mm Hg.

28. The magnetic anisotropy of colloidal crystals of graphite. A. GOETZ, A. FAESSLER AND A. B. FOCKE, *California Institute of Technology.*—A method has been developed which permits one to measure the magnetic susceptibilities of small single crystals down to ultramicroscopic sizes, with regard to their crystallographic orientation. The process can be applied to all crystalline substances showing magnetic anisotropies, (e.g., Sb, Bi and graphite). In case of graphite, the Ceylon-mineral is carefully purified which process proves to be important in order to obtain single crystalline particles of high perfection. This powder is suspended in a liquid solution of agar in order to settle. The process of settling takes place in the field of a strong magnet which orients each particle with regard to its most paramagnetic axis. Then the agar-solution is solidified by cooling, thus fixing each particle in its position, and forming a specimen similar to a large single crystal in which each particle is parallel to, but separated from its neighbour. The magnetic anisotropies of such single crystals are remarkably large, partly due to the absence of distortion and occlusion of impurities, both occuring in natural crystals. Whereas $\chi_{\parallel}/\chi_{\perp}$ has been measured in natural crystals from 1:4 to 1:7, values of 1:18 have been obtained from colloidal crystals. It is furthermore possible to determine the critical size of the particles below which the crystal diamagnetism begins to depend on the dimensions of the crystal (below 10^{-4} cm). It is hoped that experiments of the type described will permit the direct measurement of the mean free path of the "free" electrons in crystals.

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